JOURNAL

OF

THE CHEMICAL SOCIETY.

Committee of Publication:

Chairman: N. V. SIDGWICK, M.A., Sc.D., F.R.S.

M. P. APPLEBEY, M.A., B.Sc.
H. B. BAKER, C.B.E., D.Sc., F.R.S.
H. BASSETT, D.Sc., Ph.D.
H. V. A. BRISCOE, D.Sc.
F. G. DONNAN, C.B.E., M.A., F.R.S.
H. W. DUDLEY, O.B.E., M.Sc., Ph.D.
U. R. EVANS, M.A.
J. J. FOX, O.B.E., D.Sc.
C. S. GIBSON, O.B.E., M.A.
R. W. GRAY, O.B.E., Ph.D.
A. J. GREENAWAY, F.I.C.
T. A. HENRY, D.Sc.
C. K. INGOLD, D.Sc., F.R.S.
J. KENYON, D.Sc.
H. KING, D.Sc.
H. MCCOMBIE, D.S.O., M.C., D.Sc.
T. S. MOORE, M.A., B.Sc.
G. T. MORGAN, O.B.E., D.Sc., F.R.S.
K. J. P. ORTON, M.A., F.R.S.
J. R. PARTINGTON, M.B.E., D.Sc.
J. C. PHILIP, O.B.E., D.Sc., F.R.S.
T. S. PRICE, O.B.E., D.Sc., F.R.S.
F. L. PYMAN, D.Sc., F.R.S.
E. K. RIDEAL, M.A., Ph.D.
R. ROBINSON, D.Sc., F.R.S.
J. F. THORPE, C.B.E., D.Sc., F.R.S.

Editor:
CLARENCE SMITH, D.Sc.

Assistant Editor:
A. D. MITCHELL, D.Sc.

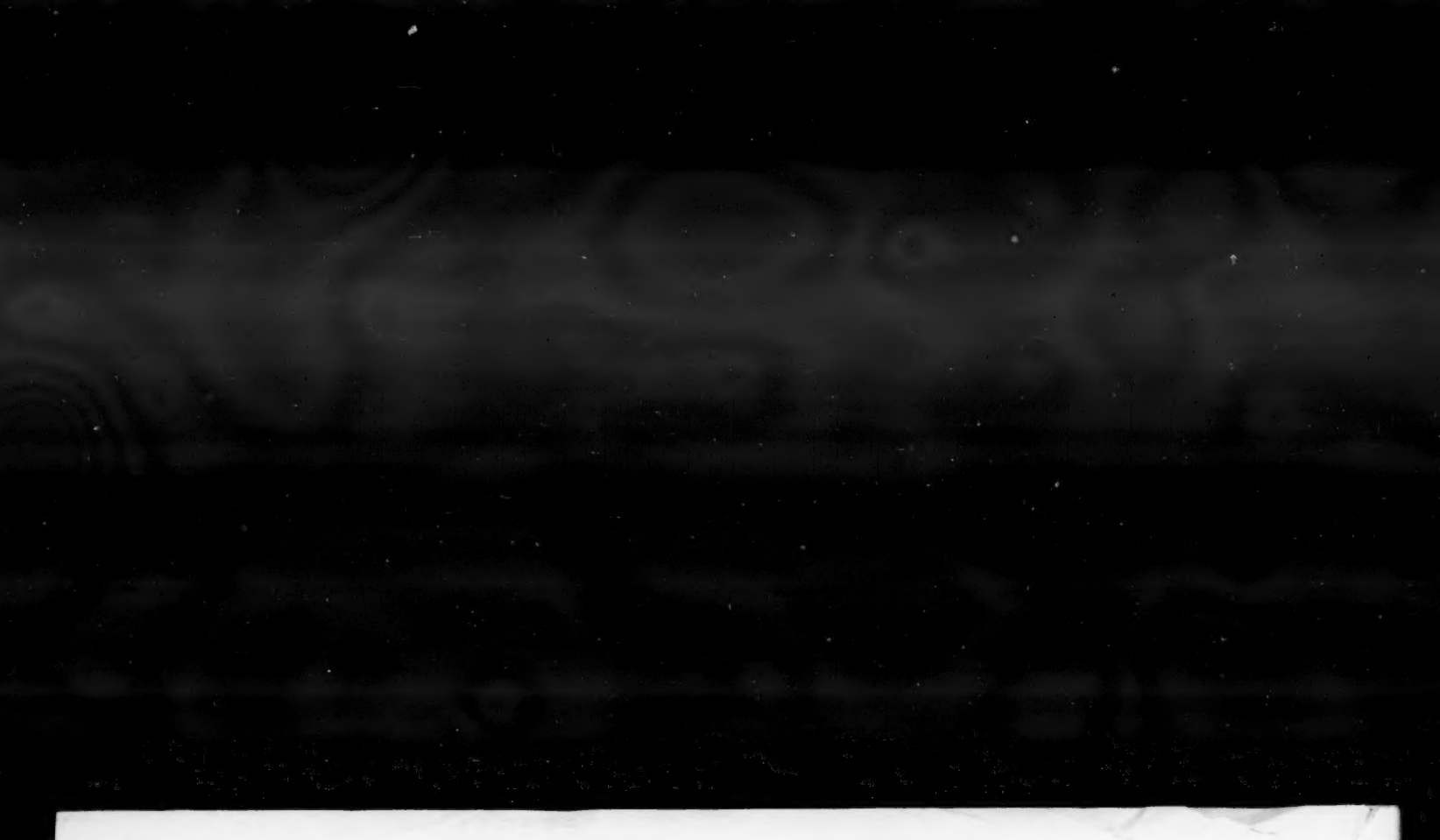
Indexer:
MARGARET LE PLA, B.Sc.

1927. Pt 1

LONDON:
GURNEY & JACKSON, 33, PATERNOSTER ROW, E.C. 4.
1927.

0474.d.

PRINTED IN GREAT BRITAIN BY
RICHARD CLAY & SONS, LIMITED
BUNGAY, SUFFOLK.



State Library
R 11 1927

130 Pt 1

JOURNAL
OF
THE CHEMICAL SOCIETY

CONTAINING

PAPERS COMMUNICATED TO THE SOCIETY

JANUARY 1927

President:
H. Brereton Baker, C.B.E., D.Sc., F.R.S.

Vice-Presidents
WHO HAVE FILLED THE OFFICE OF PRESIDENT:

H. E. Armstrong, LL.D., Ph.D., F.R.S.
Arthur W. Crossley, C.M.G., C.B.E., F.R.S.
P. F. Frankland, C.B.E., LL.D., Sc.D., F.R.S.
W. H. Perkin, Sc.D., LL.D., F.R.S.
Alexander Scott, M.A., D.Sc., F.R.S.
W. P. Wynne, D.Sc., F.R.S.

Vice-Presidents:
J. B. Cohen, D.Sc., Ph.D., F.R.S.
A. J. Greenaway, F.I.C.
James C. Philip, O.B.E., D.Sc., F.R.S.
Sir Robert Robertson, K.B.E., D.Sc., F.R.S.
R. Robinson, D.Sc., F.R.S.
N. V. Sidgwick, M.A., Sc.D., F.R.S.

Treasurer:
J. F. Thorpe, C.B.E., D.Sc., F.R.S.

Secretaries:
T. Slater Price, O.B.E., D.Sc., F.R.S.
C. S. Gibson, O.B.E., M.A., M.Sc.

Foreign Secretary:
F. G. Donnan, C.B.E., M.A., Ph.D., F.R.S.

Ordinary Members of Council:
H. Bassett, D.Sc., Ph.D.
D. R. Boyd, D.Sc., Ph.D.
O. L. Brady, D.Sc., B.A.
H. V. A. Briscoe, D.Sc.
A. E. Dunstan, D.Sc.
F. A. Freeth, O.B.E., D.Sc., F.R.S.
F. W. Gamble.
R. Whytlaw Gray, O.B.E., Ph.D.
J. Kenyon, D.Sc.
B. Lambert, M.A.
T. S. Moore, M.A., B.Sc.
T. J. Nolan, B.A., D.Sc.
K. J. P. Orton, M.A., Ph.D., F.R.S.
R. H. Pickard, D.Sc., Ph.D., F.R.S.
B. D. Porritt, M.Sc.
F. L. Pyman, D.Sc., Ph.D., F.R.S.
G. Stubbs, C.B.E.
F. J. Wilson, D.Sc., Ph.D.

Assistant Secretary:
S. E. Carr.

Librarian:
F. W. Clifford.

Burlington House, London, W. 1
Telephone—Gerrard 6322.

LONDON: GURNEY AND JACKSON
33, PATERNOSTER ROW, E.C. 4

Printed in Great Britain by Richard Clay & Sons, Ltd.,
Bungay, Suffolk.

Committee of Publication:

Chairman: N. V. Sidgwick, M.A., Sc.D., F.R.S.

H. B. Baker, C.B.E., D.Sc., F.R.S.
E. C. C. Baly, C.B.E., F.R.S.
H. Bassett, D.Sc., Ph.D.
H. V. A. Briscoe, D.Sc.
F. G. Donnan, C.B.E., M.A., F.R.S.
H. W. Dudley, O.B.E., M.Sc., Ph.D.
U. R. Evans, M.A.
J. J. Fox, O.B.E., D.Sc.
C. S. Gibson, O.B.E., M.A.
R. W. Gray, O.B.E., Ph.D.
A. J. Greenaway, F.I.C.
T. A. Henry, D.Sc.
C. K. Ingold, D.Sc., F.R.S.
H. King, D.Sc.
H. McCombie, D.S.O., M.C., D.Sc.
W. H. Mills, Sc.D., F.R.S.
T. S. Moore, M.A., B.Sc.
G. T. Morgan, O.B.E., D.Sc., F.R.S.
K. J. P. Orton, M.A., F.R.S.
J. R. Partington, M.B.E., D.Sc.
J. C. Philip, O.B.E., D.Sc., F.R.S.
R. H. Pickard, D.Sc., F.R.S.
T. S. Price, O.B.E., D.Sc., F.R.S.
F. L. Pyman, D.Sc., F.R.S.
R. Robinson, D.Sc., F.R.S.
J. F. Thorpe, C.B.E., D.Sc., F.R.S.

Editor:
Clarence Smith, D.Sc.

Assistant Editor:
A. D. Mitchell, D.Sc.

Indexer:
Margaret Le Pla, B.Sc.

The Chemical Society, founded in 1841 and first granted a Royal Charter in 1848, now numbers over 4,000 Fellows. Each Fellow is entitled to receive one copy of the Journal and of such other publications of the Society as the Council may determine, to use the Library, either directly or through the post, and to take part in the meetings of the Society. Experimental work is assisted by grants from the Research Fund. Fellows are also allowed certain privileges by kindred societies.

The publications include the *Journal*, containing papers communicated to the Society, the *Abstracts*, covering the current literature in pure Chemistry, the *Indexes*, and the *Annual Reports* on the progress of Chemistry.

The *Library* contains 28,424 volumes, among which there are 293 current journals, covering applied as well as pure chemistry. It is open each week day at 10 a.m. and closes at 9 p.m., except on Saturday, when the closing hour is 5 o'clock.

The *Meetings*, including those devoted to special lectures, number about 18 annually. Fellows resident outside London may read before British Local Sections of the Society of Chemical Industry papers intended for subsequent publication in the Journal of the Chemical Society.

The annual subscription is £3. Those desiring to become Fellows of the Society should apply for further information to the Secretaries, Burlington House, London, W. 1.

JOURNAL

OF

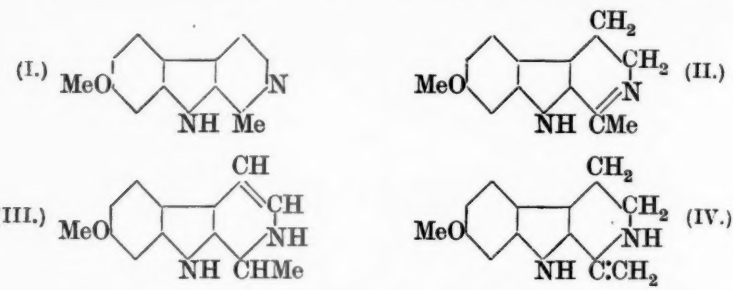
THE CHEMICAL SOCIETY.

I.—*Harmine and Harmaline. Part IX. A Synthesis of Harmaline.*

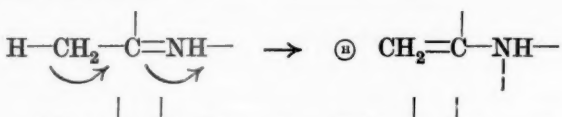
By Richard Helmuth Fred Manske, William Henry Perkin, jun., and Robert Robinson.

In earlier parts of this series of papers several syntheses of derivatives or degradation products of the *harmala* alkaloids have been recorded and the evidence afforded by the syntheses of *apo*harmine (Part VII; Lawson, Perkin, and Robinson, J., 1924, **125**, 626), norharman (Part V; Kermack, Perkin, and Robinson, J., 1921, **119**, 1619), harman (Part IV; Perkin and Robinson, J., 1919, **115**, 968), and *N*-methyltetrahydronorharmine (Part VI; Kermack, Perkin, and Robinson, J., 1922, **121**, 1890) amply suffices to determine the constitution of harmine (I). Some details of the structure proposed for harmaline (II), however, awaited confirmation by a synthetical method and for this reason, in planning the present investigation, although harmine and harmaline are interconvertible, we decided to attempt the synthesis of harmaline in the first place and, furthermore, we hoped to employ a series of reactions such that a successful outcome of the work would have a real bearing on the constitutional problem. After numerous attempts in other directions, only one of which is mentioned in this communication, the synthesis of harmaline has been effected and in such a manner (see below) as strongly to support the adoption of the expression (II) and to exclude (III) as a representation of the constitution of this base. Apart from (II), the synthesis is consistent only with the formula (IV), and we take this opportunity of pointing out that the reactions of harmaline may be satisfactorily interpreted on the hypothesis that (II) and (IV) are tautomerides, the crystallised base being probably (II). It has already been shown (Part VIII; Nishikawa, Perkin, and Robinson, J., 1924, **125**, 657) that methylharmaline and acetylharmaline are

N-substituted derivatives of (IV) and therefore the nucleus exhibits little disinclination to assume this configuration, which probably

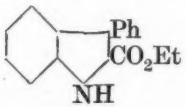


comes into play in the characteristic reactions of harmaline with diazonium salts and with benzaldehyde. On the other hand, the tertiary basic character required by formula (II) is exhibited towards methyl iodide and other alkylating agents and all analogies (compare, for example, the salt formation of ethyl β-aminocrotonate, 1-benzylidene-*N*-methyltetrahydro*iso*quinoline, *iso*papaverine, methylenedihydroquinolines, and of other anhydronium bases) indicate that the double bond in a salt of harmaline is invariably in the position illustrated in (II). We do not conceive the interchange between (II) and (IV) as a direct one but rather as a process dependent on the presence of hydrogen ions, the decomposition of a kation in two directions being responsible for any equilibrium which may be established. The electronic changes and fission involved are represented in the annexed scheme.

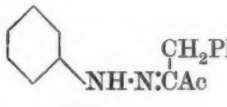


Turning to the detail of the synthetical work, the feasibility of our plan in main outline was clearly indicated when we found in a favourable case that E. Fischer's synthesis of indole derivatives could be applied to the monophenylhydrazone of an α-diketone, a member of a class of substances which are very readily accessible in great variety through the Japp–Klingemann reaction (*Ber.*, 1888, **21**, 549; *Annalen*, 1888, **247**, 218). The advantages of this procedure are manifold; indole derivatives can be prepared which are difficult or impossible to obtain in other ways, but apart from this, the Japp–Klingemann reaction gives excellent yields and the stage of reduction of the diazonium salt to a hydrazine is eliminated. Ethyl α-acetyl-β-phenylpropionate condenses directly with

benzenediazonium chloride in alkaline-alcoholic solution with extrusion of the acetyl group, and the product, after hydrolysis and treatment with alcoholic hydrogen chloride, yields *ethyl 3-phenylindole-2-carboxylate* (V). On the other hand, an alkaline solution of sodium α-acetyl-β-phenylpropionate and benzenediazonium chloride affords, with extrusion of the carboxyl group, *α-phenylbutane-βγ-dione β-phenylhydrazone* (VI). Boiling concentrated hydrochloric acid induces indole cyclisation of this substance to *2-acetyl-3-phenylindole* (VIII), which yields 3-phenylindole on fusion with sodium hydroxide.



(V.)



(VI.)

(VII.)

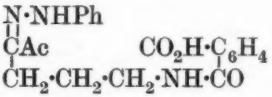
The method was then extended to the preparation of a 2-acetyl-3-β-aminoethylindole derivative and, as appeared in the sequel, we fortunately selected the phthaloyl residue for the protection of the amino-group. Ethyl δ-phthalimido-α-acetylvalerate,

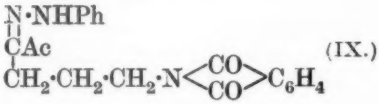
$$C_6H_4(CO)_2N\cdot CH_2\cdot CH_2\cdot CH_2\cdot CHAc\cdot CO_2Et$$

(Gabriel, *Ber.*, 1909, **42**, 1242), was hydrolysed by cold aqueous-alcoholic sodium hydroxide with the formation of the salt

$$CO_2Na\cdot C_6H_4\cdot CO\cdot NH\cdot CH_2\cdot CH_2\cdot CH_2\cdot CHAc\cdot CO_2Na,$$

and this coupled in the alkaline solution with benzenediazonium chloride, losing the carboxyl group and yielding, after acidification, *ζ-o-carboxybenzamidohexane-βγ-dione γ-phenylhydrazone* (VIII). This phthalamic acid was easily converted into the corresponding phthalimide (IX) by means of acetic anhydride.

(VIII.)


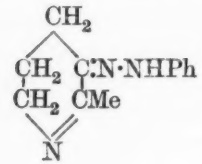


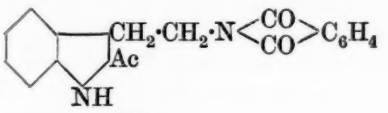
(IX.)

At this stage, serious difficulty was encountered in the course of attempts to induce the indole transformation of these phenylhydrazones. The compound (VIII) exhibits a marked tendency to split off phthalic acid with formation of a remarkable tetrahydropicoline derivative (X). This substance is a strong, stable base forming intensely yellow salts and it is best prepared from the phthalamic acid derivative by the action of hydrogen chloride in hot acetic acid solution; further representatives of this series have been similarly obtained and are described in the experimental section. An interesting property of the base is its stability to acids and so far as we are aware it cannot be converted into an

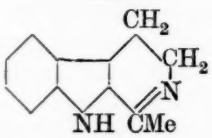
indole derivative under the influence of acids or reagents such as zinc chloride. In the light of the theory of the mechanism of the Fischer indole synthesis (Robinson and Robinson, J., 1918, **113**, 639; 1924, **125**, 827), this means that the substance does not occur in the phase containing the group NHPh·NH·C=C—, and it is not unreasonable to attribute this circumstance to the plastic, semi-aromatic character of the system NHPh·N:C·C:N—. In such assemblages there is a reduction of unsaturated character and a stability factor which operates against the transfer of the unsaturation to any external group in a tautomeric process.

Further evidence that the hydrazone complex has been modified in character by the associated imino-centre is supplied by the resistance which the base exhibits to hydrolysis. The formation of (X) from (VIII) is doubtless facilitated by, or is even entirely

(X.) 



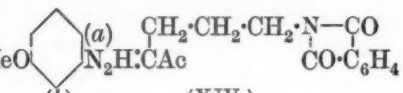
(XI.)

(XII.) 

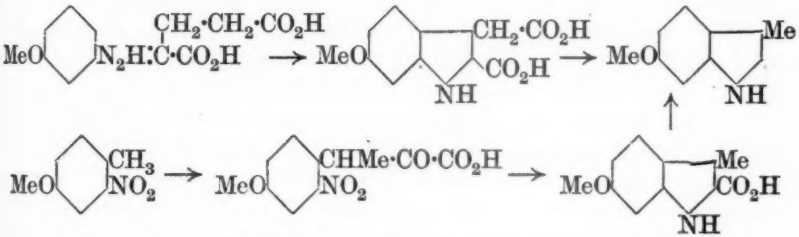
due to, the formation of an intermediate product containing the group ·CMe(OH)·N·CO—, and if the nitrogen of the amide group carried no hydrogen atom this preliminary ring closure would, of course, be avoided. Actually it was found possible to obtain the corresponding indole derivative (XI) from (IX) by the use of boiling alcoholic hydrochloric acid, and no other reagent, in our experience, is able to bring about the transformation.

In order to obtain *harmalan*, the name by which we propose to designate *des*methoxyharmaline (since *des*methoxyharmine is termed harman), it was necessary to remove the phthaloyl group from (XI) by hydrolysis, and in this connexion a method was devised which is likely to prove generally serviceable in synthetical investigations involving the use of phthalimide derivatives. The action of hydrazine hydrate in hot alcoholic solution on (XI), followed by treatment of the product with hydrochloric acid, yields, quite smoothly, phthalhydrazide, $C_6H_4(CO)_2(NH)_2$, which is insoluble, and a solution of harmalan hydrochloride. Ing and Manske (compare J., 1926, 2348) have shown that the process is generally applicable as the final stage in Gabriel's synthesis of amines.

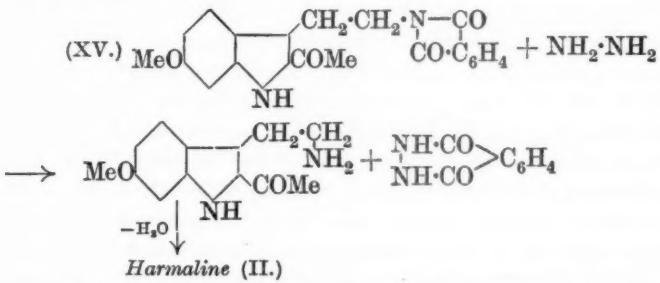
Harmalan (XII) crystallises with $10H_2O$ and on oxidation with chromic acid yields harman (aribine, loturine) (XIII).



Replacing benzenediazonium chloride by *m*-methoxybenzenediazonium chloride in the above series of reactions, we obtained a methoxy-derivative of the phthalamic acid (VIII) and then by dehydration the phthalimide derivative (XIV). In this substance, the indole ring might be closed in either of the positions (*a*) and (*b*), but Kermack, Perkin, and Robinson (J., 1921, **119**, 1614) have realised the following scheme, proving not only that closure in position (*a*) is favoured, but also that the reaction involves no alteration in the orientation of the substituents in the benzene ring.



It was found very difficult to transform the hydrazone (XIV) into an indole derivative, but ultimately the change was brought about with the help of *n*-butyl-alcoholic hydrogen chloride. The product (XV) was then converted into harmaline (II) by the hydrazine method as illustrated below.



Harmaline (II.)

The synthetic base was found to be identical with natural harmaline in all respects; the less pure residues were oxidised to harmine, indistinguishable from a specimen derived from *Peganum harmala*.

Although this memoir does not quite complete the account of

our investigations in the group of the *harmala* alkaloids, we feel that the present opportunity should be taken in order to pay a tribute of appreciation to the pioneer worker in this field of chemistry. Our researches owe much to the difficult experimental investigations of Otto Fischer which preceded them.

Experimental.

γ-Phthalimidobutyronitrile, $C_6H_4(CO)_2N{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CN$.—In the course of our earlier experiments considerable quantities of this nitrile were prepared with the object of attempting the reduction of the substance to γ-phthalimidobutaldehyde. The latter stage was not accomplished satisfactorily, but the direct replacement of bromine by the cyano-group in γ-bromopropylphthalimide was effected by the use of anhydrous methyl-alcoholic sodium cyanide. This transformation was attempted by Gabriel (*Ber.*, 1889, **22**, 3337) without success and it is certain that the following conditions cannot be greatly varied. Anhydrous hydrogen cyanide (7 c.c.) and sodium iodide (0·5 g.) were added to a solution of sodium methoxide (from 3 g. of sodium) in dry methyl alcohol (50 c.c.); the sodium cyanide was precipitated in a finely-divided condition. After the introduction of γ-bromopropylphthalimide (27 g.), the mixture was refluxed for 2 hours and most of the alcohol removed by distillation. The product, isolated after the addition of water, crystallised from alcohol (20 c.c.) (charcoal) in rhombohedra (yield, 12—16 g.). This pale brown material is sufficiently pure for many purposes and one recrystallisation from alcohol gives the pure nitrile, m. p. 81°. The substance has been previously obtained by Gabriel (*Ber.*, 1889, **22**, 3337) from potassium phthalimide and γ-bromobutyronitrile.

3-*Phenylindole*-2-*carboxylic Acid* (formula as V).—The phenylhydrazone of phenylpyruvic acid (Wislicenus, *Ber.*, 1887, **20**, 593) may be conveniently prepared by the following application of the Japp-Klingemann reaction. A solution of sodium hydroxide (12 g.) in water (30 c.c.) was added to one of ethyl α-acetyl-β-phenylpropionate (22 g.) in alcohol (150 c.c.) and, without delay, a solution of benzenediazonium chloride (from 9·3 g. of aniline and 50 c.c. of concentrated hydrochloric acid) was introduced, causing the precipitation of a heavy brown oil. A few minutes later the product was precipitated by the addition of water, washed by decantation, and, as it did not solidify, was at once hydrolysed by means of alcoholic sodium hydroxide on the steam-bath. The acid obtained on acidification was crystallised from aqueous alcohol, yielding 20 g. of a product, m. p. 160° (Wislicenus, *loc. cit.*, gives m. p. 161°).

A solution of the hydrazone (26 g.) in alcohol (75 c.c.) was rapidly

saturated with hydrogen chloride and then refluxed for ½ hour; ammonium chloride separated. The resinous mass obtained on the addition of water afforded, on solution in hot alcohol and cooling, about 2 g. of *ethyl 3-phenylindole-2-carboxylate* (V). This ester crystallised from alcohol in colourless rhombohedra, m. p. 137—138° (Found: C, 76·8; H, 5·8; N, 5·3. $C_{17}H_{15}O_2N$ requires C, 77·0; H, 5·7; N, 5·3%). The alcoholic mother-liquor, after the separation of the ester, was made strongly alkaline by means of sodium hydroxide and heated on the steam-bath for an hour. Water then precipitated some 3-phenylindole, identified by its m. p. (87°) and by colour reactions, whilst the alkaline filtrate from this, on acidification, gave *3-phenylindole-2-carboxylic acid*, which was dried (10 g.) and crystallised from benzene. The colourless clusters of needles, m. p. 186° (Found: C, 75·3; H, 4·7; N, 5·8. $C_{15}H_{11}O_2N$ requires C, 75·9; H, 4·6; N, 5·9%), lose carbon dioxide, on heating, with formation of 3-phenylindole.

α-Phenylbutane-βγ-dione β-Phenylhydrazone (VI).—A solution of sodium hydroxide (9 g.) in water (25 c.c.) was added to ethyl α-acetyl-β-phenylpropionate (44 g.) in alcohol (50 c.c.). Shortly after the formation of a semi-solid gelatinous mass, water (500 c.c.) was added and the mixture stirred until only a small amount of oil remained unacted upon. This was removed by passing the liquid through a wet filter and a solution of benzenediazonium chloride (from 18 g. of aniline, 13 g. of sodium nitrite, and 50 c.c. of concentrated hydrochloric acid) was introduced. The addition of crystallised sodium acetate (100 g.) caused the rapid precipitation of the phenylhydrazone, which was carried to the surface by the liberated carbon dioxide and was collected, washed with water, aqueous sodium carbonate, and then again with water (yield after drying, 42—44 g.). The substance, which may be distilled in small quantities undecomposed under diminished pressure, crystallises from alcohol or benzene in glistening, pale yellow plates, m. p. 108°, and is readily soluble in chloroform (Found: C, 75·5; H, 6·3; N, 11·2. $C_{16}H_{16}ON_2$ requires C, 76·2; H, 6·3; N, 11·1%).

α-Phenylbutane-βγ-dione β-m-nitrophenylhydrazone and *β-2:5-dimethoxyphenylhydrazone* were obtained in the same way as the preceding compound, the appropriate derivative being substituted for aniline. The former is sparingly soluble in acetic acid, from which it separates in yellow needles, m. p. 146° (Found: C, 64·9; H, 5·1; N, 14·5. $C_{16}H_{15}O_3N_3$ requires C, 64·6; H, 5·0; N, 14·1%). The latter crystallises from alcohol in greenish-yellow needles, m. p. 107° (Found: C, 69·5; H, 6·5; N, 9·2. $C_{18}H_{20}O_3N_2$ requires C, 69·2; H, 6·4; N, 9·0%). In both cases, the yield was 80% of that theoretically possible.

2-Acetyl-3-phenylindole (VII).—α-Phenylbutane-βγ-dione β-phenylhydrazone (25·2 g.) was added in one portion to boiling hydrochloric acid (75 c.c.; *d* 1·16), and the mixture then boiled for 15 minutes. The oil precipitated on the addition of a large volume of water was washed by decantation and soon crystallised (dried, 23 g.). The substance was crystallised from alcohol and then from benzene, being obtained in stout, pale yellow prisms, m. p. 151° (Found: C, 81·4; H, 5·8; N, 6·1. $C_{16}H_{13}ON$ requires C, 81·7; H, 5·5; N, 6·0%). The crude product may also be conveniently purified by distillation under diminished pressure. On fusion with sodium hydroxide and a little water for a few minutes at a high temperature, 3-phenylindole was obtained; it was identified by the m. p. (87°) of a mixture and by comparison with an authentic specimen.

Ethyl δ-Phthalimido-α-acetylvalerate.—This ester has been described by Gabriel (*loc. cit.*). Since relatively large quantities of it were required, we have studied the optimum conditions for the preparation. After sodium (24 g.) had been dissolved in anhydrous alcohol (300 c.c.), ethyl acetoacetate (140 g.) and γ-bromopropylphthalimide (268 g.) (Gabriel and Weiner, *Ber.*, 1888, **21**, 2671; compare Ing and Manske, this vol., p. 2348) were successively introduced and the mixture was refluxed for 2 hours. The greater part of the alcohol was then removed by distillation and the residue added to water (2000 c.c.). The oil crystallised and was collected, washed with much cold water and dried. The yield was uniformly 300—310 g. and in this form the substance is sufficiently pure to be employed for the purposes mentioned below. A specimen crystallised from benzene–light petroleum had m. p. 64° (Gabriel, *loc. cit.*, gives 65°) (Found: C, 64·8; H, 6·0; N, 4·3. Calc. for $C_{17}H_{19}O_5N$: C, 64·4; H, 6·0; N, 4·4%).

ζ-o-Carboxybenzamidohexane-βγ-dione γ-Phenylhydrazone (VIII).—A solution of sodium hydroxide (25 g.) in water (100 c.c.) was added to one of ethyl δ-phthalimido-α-acetylvalerate (95 g.) in alcohol (100 c.c.), the temperature being kept below 10°. After 5 hours, cold water (1000 c.c.) was added and on the following day the solution was shaken with a little animal charcoal and filtered, and crystallised sodium acetate (200 g.) was dissolved in it. The liquid was then mechanically agitated during the introduction of a solution of benzenediazonium chloride prepared from aniline (28 g.), concentrated hydrochloric acid (150 c.c.), and sodium nitrite (21 g.) dissolved in water (50 c.c.). A brown, pasty mass was immediately formed and carried to the surface by the liberated carbon dioxide. Stirring was continued for an hour and after the solution had been rendered strongly acid by means of

hydrochloric acid the pale brown precipitate was collected and washed with water. The crude product was dissolved as far as possible in aqueous sodium hydroxide (1000 c.c. of 4%) and was reprecipitated after the solution had been treated with charcoal and filtered (dried, 90—95 g.). After crystallisation from acetone, almost colourless needles, melting with loss of water at 156—157°, were obtained (Found: C, 65·4; H, 6·1; N, 11·3. $C_{20}H_{21}O_4N_3$ requires C, 65·4; H, 5·7; N, 11·4%). This acid is sparingly soluble in most organic solvents in the cold.

ζ-Phthalimidohexane-βγ-dione γ-Phenylhydrazone (IX).—The acid just described was at first converted into an anhydro-derivative by heating it at 180° under diminished pressure (yield, 10—20%). The following procedure is much more satisfactory, the yield being 70% of that theoretically possible. Carboxybenzamidohexanedione phenylhydrazone (37 g.) was added to an equal weight of boiling, freshly-distilled acetic anhydride, and the source of heat removed. When the exothermic reaction ceased, the mixture was boiled for 5 minutes, allowed to cool to 80°, and 95% alcohol (40 c.c.) then added. Crystallisation was induced by inoculation and after cooling in ice-water the solid was collected and washed with alcohol until the filtrate was colourless (dried, 24—28 g.). This material, m. p. 168—170°, is pure enough for most purposes. The substance crystallises from acetic acid in pale yellow needles, m. p. 172° (Found: C, 68·7; H, 5·7; N, 11·5. $C_{20}H_{19}O_3N_3$ requires C, 68·8; H, 5·4; N, 12·0%). It is but sparingly soluble in hot acetic acid and extremely sparingly soluble in boiling alcohol.

5-Keto-6-methyl-2 : 3 : 4 : 5-tetrahydropyridine 5-Phenylhydrazone (X).—A stream of dry hydrogen chloride was led during 10 minutes through a boiling solution of carboxybenzamidohexanedione phenylhydrazone (37 g.) in acetic acid (75 c.c.). The hydrochloride which separated on cooling was collected and washed with cold acetic acid (dried, 20 g.). The corresponding base, set free by means of aqueous sodium hydroxide, crystallised from benzene in pale yellow, almost rectangular prisms, m. p. 134—135°, which effloresce on exposure to air and even then contain benzene (Found: C, 74·9; H, 7·7; N, 17·7. $C_{12}H_{15}N_3,\frac{1}{2}C_6H_6$ requires C, 75·0; H, 7·5; N, 17·5%); it is readily soluble in alcohol, moderately readily soluble in benzene, and sparingly soluble in light petroleum. The *hydrochloride* is sparingly soluble in water and crystallises in brilliant yellow leaflets, m. p. 286° (decomp.) (Found: C, 61·7; H, 7·1; N, 17·6; Cl, 14·7. $C_{12}H_{15}N_3,HCl$ requires C, 60·6; H, 6·8; N, 17·7; Cl, 14·9%). The solutions of this salt and of other salts of the base and of the analogues described below are bright yellow and unaffected by nitrous acid. Addition of zinc dust to an acid

solution causes decoloration and a diazotisable amine is produced. The filtrate from the original preparation contained phthalic acid but no ammonium salt. Owing to the unusual difficulty experienced in getting satisfactory or consistent results in the estimation of carbon, two further examples of the reaction were investigated and the combined evidence as to the composition of these curious bases is decisive.

ζ-o-Carboxybenzamidohexane-βγ-dione γ-m-Chlorophenylhydrazone (formula as VIII).—This substance was obtained in the same way as the corresponding phenylhydrazone on substituting *m*-chloroaniline for aniline. The crude product was purified by reprecipitation from a solution in dilute aqueous sodium hydroxide, and the substance separated from acetone and then from alcohol as a pale yellow, crystalline powder, m. p. 210° (decomp.) (Found : C, 60·4; H, 5·2; N, 10·5; Cl, 8·5. $C_{20}H_{20}O_4N_3Cl$ requires C, 59·7; H, 5·0; N, 10·4; Cl, 8·8%). This acid is sparingly soluble in most organic solvents.

5-Keto-6-methyl-2 : 3 : 4 : 5-tetrahydropyridine 5-m-*Chlorophenylhydrazone* (formula as X).—Carboxybenzamidohexanedione chlorophenylhydrazone (10 g.), dissolved in boiling acetic acid (20 c.c.), was submitted to the action of a stream of hydrogen chloride for 5 minutes, the resulting hydrochloride crystallising, even from the hot solution. The related base, isolated from an aqueous solution which had been treated with charcoal (yield, 5 g.), crystallised from benzene in yellow prisms, m. p. 161° (Found : N, 17·7; Cl, 14·6. $C_{12}H_{14}N_3Cl$ requires N, 17·8; Cl, 15·1%). The *hydrochloride* separates from boiling aqueous solutions in glistening, yellow leaflets.

5-Keto-6-phenyl-2 : 3 : 4 : 5-tetrahydropyridine 5-Phenylhydrazone (formula as X).—In the preparation of this substance no serious attempt was made to purify the intermediates. The condensation of ethyl benzoylacetate (39 g.) and γ-bromopropylphthalimide (52 g.) in the presence of alcoholic sodium ethoxide gave 74 g. of an oily product which was hydrolysed by means of aqueous-alcoholic sodium hydroxide and subsequently coupled with benzenediazonium chloride as in the type example. The yield of resinous hydrazone acid was 60 g. A stream of hydrogen chloride was passed into a solution of one-third of this product in its own weight of boiling acetic acid for 10 minutes. On cooling, a certain amount of the hydrochloride separated, but it was found advantageous to add water (200 c.c.), boil (charcoal), and concentrate the filtered solution to about 75 c.c. On cooling, there was a copious separation of a pale yellow, crystalline *hydrochloride*, which was collected, washed, and then decomposed with aqueous sodium hydroxide. The base (5 g.) crystallised from benzene–methyl alcohol in yellow,

prismatic needles, m. p. 146—147° (Found: C, 78·2; H, 6·9; N, 15·2. $C_{17}H_{17}N_3$ requires C, 77·6; H, 6·5; N, 15·9%).

2-Acetyl-3-β-phthalimidoethylindole (XI).—The indole cyclisation of phthalimidohexanedione phenylhydrazone does not give quite satisfactory yields under any conditions which we have employed, but the following procedure affords uniform results. A stream of dry hydrogen chloride was passed through a suspension of the hydrazone (17·5 g.) in boiling alcohol (150 c.c.) (reflux) for 45 minutes. Most of the alcohol was removed by distillation and the residue repeatedly washed with hot water. The aqueous extract contained ammonium chloride. The brown tar was dried (17 g.) and refluxed with acetone (400 c.c.) and animal charcoal (2 g.) for about 2 hours; the solution was then filtered and concentrated to a small volume. On keeping for several days, the residual pale brown syrup became semi-solid—the change may be hastened by inoculation. The crystals were collected, washed with cold acetone, and dried (2·5—3 g.; m. p. 206—210°). The substance is very sparingly soluble in boiling acetone or alcohol and crystallises from acetic acid in small, colourless, rhombic prisms, m. p. 214° (Found: C, 72·5; H, 5·0; N, 8·4. $C_{20}H_{16}O_3N_2$ requires C, 72·3; H, 4·8; N, 8·4%). The combined mother-liquors from four such preparations were worked up for harman (see below).

Harmalan (XII).—A mixture of acetylphthalimidoethylindole with its own weight of hydrazine hydrate and ten times its weight of alcohol was boiled for 20 minutes and the resulting clear solution, acidified with hydrochloric acid, was boiled for a further 20 minutes and filtered through a layer of charcoal. An excess of sodium hydroxide was added to the pale yellow, strongly fluorescent filtrate, and, after cooling, the semi-crystalline base was collected, washed, and dried (weight about ½ of the phthalimido-derivative taken). Harmalan crystallises best from water or from 10% alcohol in very pale yellow needles and after two recrystallisations has m. p. 182—183°, if previously dried for several hours at 75°. This product lost 48·9% at 100° in a vacuum (Found in anhydrous material: C, 78·1; H, 6·6; N, 14·8. $C_{12}H_{12}N_2,10H_2O$ requires H_2O, 49·4%. $C_{12}H_{12}N_2$ requires C, 78·3; H, 6·5; N, 15·2%). Solutions of salts of harmalan are pale yellow and exhibit a blue fluorescence, which is intensified on the addition of alcohol. The solution in concentrated sulphuric acid is non-fluorescent.

Harman (XIII).—Harmalan chromate is a sparingly soluble, brown powder and on boiling with dilute sulphuric acid some harman is produced, although the yield is poor. Harman has been prepared in this way from pure harmalan, but a larger quantity became available from residues. The mother-liquors obtained in

the preparation of acetylphthalimidoethylindole were freed from acetone on the steam-bath and the tar was extracted with boiling alcohol (150 c.c.). After several days, the alcohol was decanted, the resin mixed with hydrazine hydrate (25 g.) and refluxed for 1 hour with alcohol (100 c.c.), and the resulting solution diluted with water (500 c.c.), filtered (charcoal), and acidified. The precipitated phthalhydrazide was removed (charcoal again), and the pale brown filtrate rendered strongly alkaline by the addition of sodium hydroxide. The precipitated base (about 7 g.) was collected, dissolved in dilute sulphuric acid, and a slight excess of sodium dichromate added to the solution, which was then boiled for several hours. The sparingly soluble chromate gradually disappeared as oxidation proceeded. The liquid was rendered alkaline by means of sodium hydroxide and filtered hot, and the residue extracted thrice with boiling water. The combined filtrate and extracts deposited, on cooling, sand-coloured needles, m. p. 210—215° (about 1·0 g.). One crystallisation from 5% alcohol raised the m. p. to 237°, which is the m. p. of harman (Hopkins and Cole, *J. Physiol.*, 1903, **29**, 451, give 238° as the m. p. of the base, $C_{12}H_{10}N_2$, subsequently shown to be harman; compare also Perkin and Robinson, J., 1919, **115**, 967, and Späth, *Monatsh.*, 1919, **40**, 351, who give 238° and 237—238°, respectively) (Found: N, 15·0. Calc. for $C_{12}H_{10}N_2$: N, 15·3%). The base exhibited the characteristic properties of harman, in particular the bluish-violet fluorescence of the aqueous solutions of its salts.

ζ-o-Carboxybenzamidohexane-βγ-dione β-m-Methoxyphenylhydrazone (formula as VIII).—A solution of sodium δ-*o*-carboxybenzamido-α-acetylvalerate, obtained exactly as described above from ethyl δ-phthalimido-α-acetylvalerate (95 g.), in which crystallised sodium acetate (200 g.) had been dissolved was stirred, and a solution of *m*-methoxybenzenediazonium chloride (from 37 g. of *m*-anisidine, 150 c.c. of concentrated hydrochloric acid, and 21 g. of sodium nitrite) gradually introduced. The precipitated brown semi-solid hydrazone adhered to the sides of the vessel and was washed by decantation and dried (95—100 g.). The substance was employed in this form for the next stage. It may be purified by solution in aqueous sodium carbonate (charcoal) and reprecipitation; crystallised from much ethyl acetate and again from alcohol, it then forms orange-yellow plates, m. p. 208° (decomp.) (Found: C, 63·8; H, 5·9; N, 10·6. $C_{21}H_{23}O_3N_3$ requires C, 63·5; H, 5·8; N, 10·6%).

ζ-Phthalimidohexane-βγ-dione γ-m-Methoxyphenylhydrazone (XIV). —The above hydrazone acid (crude product, 40 g.) was added to boiling acetic anhydride (40 g.) and the solution was boiled for

5 minutes and then allowed to cool to about 80°. Alcohol (40 c.c.) was added and, on cooling and keeping, the mixture deposited a mass of crystals which were collected, washed with alcohol, and dried (28 g.; m. p. 163—165°). The substance crystallises from acetic acid in orange prisms, m. p. 167—168° (Found: C, 66·1; H, 5·6; N, 11·3. $C_{21}H_{21}O_4N_3$ requires C, 66·5; H, 5·5; N, 11·1%), and is readily soluble in chloroform.

6-*Methoxy*-2-*acetyl*-3-β-*phthalimidoethylindole* (XV).—After numerous unsuccessful attempts to prepare this indole derivative, it was found that the following procedure gave results which were at least as good as those obtained in the simpler case. A stream of hydrogen chloride was passed through a boiling solution of phthalimidohexanedione *m*-methoxyphenylhydrazone (18 g.) in *n*-butyl alcohol (150 c.c.) for 15 minutes. The solvent was then removed by distillation under diminished pressure and the brown, resinous residue was freed from impurities volatile in a current of steam. The heavy oil was repeatedly washed with hot water, dried at 100°, and treated with animal charcoal in boiling acetone solution (600 c.c.) for several hours. The filtered liquid, concentrated to a small volume, deposited the indole in the course of a few hours in almost colourless crystals (2·4 g.; m. p. 214°). The substance crystallises from acetic acid in colourless prisms, m. p. 218° (Found: C, 69·1; H, 5·2; N, 7·7. $C_{21}H_{18}O_4N_2$ requires C, 69·6; H, 5·0; N, 7·7%). Further small quantities of the substance may be obtained from the mother-liquor by renewed solution in acetone, treatment with charcoal, and concentration to a small volume.

Harmaline (II).—The removal of the phthalic residue from methoxyacetylphthalimidoethylindole was effected by the action of hydrazine as described in the section dealing with the preparation of harmalan. Harmaline, precipitated by the addition of sodium hydroxide to the acid solution, was obtained in 90% yield. Crystallisation from methyl alcohol with the aid of charcoal gave the pure base which, alone or intimately mixed with a specimen of the alkaloid derived from *Peganum harmala*, melted at 239—240° (Found in the synthetic specimen: C, 73·1; H, 7·0; N, 12·7. Calc. for $C_{13}H_{14}ON_2$: C, 72·9; H, 6·5; N, 13·1%). Comparison of the crystalline forms and fluorescent properties confirmed the identity of the specimens and nothing was observed which could differentiate them. The synthetic base was acetylated (O. Fischer, *Ber.*, 1897, **30**, 2484) and the acetyl derivative, after two crystallisations from alcohol, had m. p. 204°, alone or mixed with an authentic specimen from natural harmaline. It displayed the characteristic colour changes on heating in alcoholic aqueous hydrochloric acid solution.

Harmine (I).—In the course of the work, partly in preliminary experiments, but chiefly by working up the mother-liquors from the indole derivative preparation with hydrazine hydrate, several grams of impure and uncrystallisable harmaline were accumulated. This material was oxidised by means of chromic acid in boiling dilute sulphuric acid solution and the resulting harmine could then be crystallised from methyl alcohol with the aid of charcoal. The pale yellow needles (Found: N, 13·2. Calc. for $C_{13}H_{12}ON_2$: N, 13·3%) had m. p. 256—258°, alone or mixed with an authentic specimen of harmine, and careful comparison with the natural base also showed that the specimens were identical.

We desire to thank the Royal Commissioners for the Exhibition of 1851 for a scholarship which enabled one of us to take part in the investigation and we are also indebted to the Chemical Society for a grant which defrayed a part of the expenses incurred.

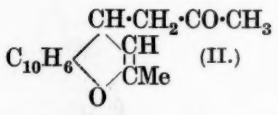
THE UNIVERSITIES OF OXFORD AND MANCHESTER. [*Received, November 15th*, 1926.]

II.—*Styrylpyrylium Salts. Part VIII. 3-Styryl Derivatives of β-Naphthapyrylium Chloride.*

By ROBERT DICKINSON and ISIDOR MORRIS HEILBRON.

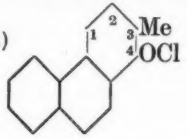
IN continuation of previous work, a study has been made of the styryl derivatives of β-naphthapyrylium chloride.

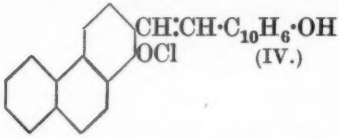
We were unable to prepare them by a method analogous to that used by Buck and Heilbron (J., 1922, **121**, 1198), since the condensation of 2-naphthol-1-aldehyde with acetone in the presence of alkali failed to give the expected β-2-hydroxy-1-naphthylvinyl methyl ketone (I). The only pure product isolated was 1-*acetonyl*-3-*methyl*-1 : 4-β-*naphthapyran* (II), which was obtained in poor yield, the bulk of the reaction product being an amorphous, yellow solid which resisted all attempts at purification.

(I.) $C_{10}H_6<^{OH}_{CH:CH\cdot COMe}$ (II.) 

Attempts were next made to prepare 3-methyl-β-naphthapyrylium chloride (III) with a view to condensing it further with aromatic aldehydes to the styryl derivatives (compare Buck and Heilbron, J., 1923, **123**, 2521), but this method failed because the condensation

of 2-naphthol-1-aldehyde with acetone in acid solution gave solely 3-(β-2′-*hydroxy*-1′-*naphthylvinyl*)-β-*naphthapyrylium chloride* (IV).

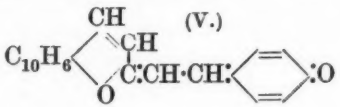
(III.) 

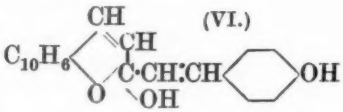


(IV.)

The salts were ultimately obtained in good yield by the condensation of 2-naphthol-1-aldehyde with styryl methyl ketones by means of dry hydrogen chloride—a somewhat unexpected result, since the corresponding condensation for styrylbenzopyrylium salts was unsatisfactory (Buck and Heilbron, J., 1922, **121**, 1198).

The styryl-β-naphthapyrylium salts are highly coloured, crystalline compounds closely resembling the 2-styrylbenzopyrylium salts in properties. For example, 3-p-*hydroxystyryl*-β-*naphthapyrylium chloride* gives a red aqueous solution which, on high dilution, becomes purplish-blue, and then, with a trace of sodium bicarbonate, cornflower-blue, and finally almost colourless. As in other similar cases, we attribute the colour change from red to blue, which is displayed only by those salts having a free hydroxyl in the 4′-position, to the formation of the quinonoid anhydro-base (V), which then hydrates to the colourless carbinol base (VI).

(V.) 

(VI.) 

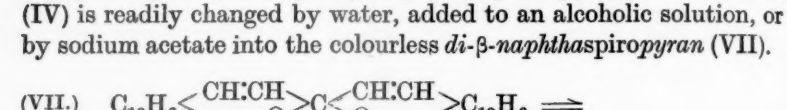
The view that the similar colour changes observed in the anthocyanidin series of salts are due to the same structural rearrangements (Buck and Heilbron, J., 1922, **121**, 1203) has been criticised by Willstätter and Schmidt (*Ber.*, 1924, **57**, 1945) as failing to account for the reactions of malvidin and œnidin chlorides, both of which, according to Willstätter, contain methoxyl groups in the 4′-position (*Annalen*, 1915, **408**, 83, 122). Such formulations are, however, supported neither by Gatewood and Robinson in the case of malvidin (J., 1926, 1959) nor by Anderson and Nabenhauer for œnidin (*J. Amer. Chem. Soc.*, 1926, **48**, 2997).

All the styryl-β-naphthapyrylium salts, on treatment with aqueous sodium hydroxide, give colourless solutions which slowly become intensely red. This colour change, which may possibly be due to fission of the pyrylium ring, is being investigated.

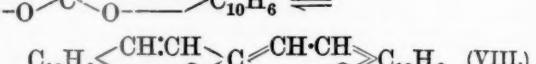
The parent substance, 3-*styryl*-β-*naphthapyrylium chloride*, is interesting in that Buck and Heilbron (*loc. cit.*) were unable to prepare the corresponding benzopyrylium salt, and further because

it differs from its derivatives : its colour in water is bright orange, and solutions in water, alcohol, and concentrated sulphuric acid all show a remarkably intense greenish-yellow fluorescence; this property is only exhibited by its derivatives in the last solvent.

3-(β-2′-Hydroxy-1′-naphthylvinyl)-β-naphthapyrylium chloride (IV) is readily changed by water, added to an alcoholic solution, or by sodium acetate into the colourless *di*-β-*naphtha*spiro*pyran* (VII).



(VII.)



(VIII.)

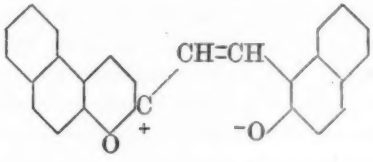
A remarkable property of this compound is its behaviour in high-boiling solvents. Its colourless solution in nitrobenzene or xylene develops, at about 100°, a purple colour which becomes progressively deeper and more intense as the temperature rises; on cooling, the reverse phenomena are observed. These changes may be repeated any number of times without the least sign of permanent decomposition. Although this behaviour resembles that accompanying the decomposition of hexa-aryl ethanes and of certain phenolic peroxides into free radicals (compare Gomberg, *Chemical Reviews*, 1925, **1**, 91), a similar decomposition does not take place here, molecular-weight determinations at high temperatures giving normal values. It is tentatively suggested that the purple colour may be due to a change in the valency distribution (VII ⇌ VIII). The possibility of both pyran rings opening in a similar manner has not been overlooked, but is regarded as unlikely.

On boiling with alcoholic potash, di-β-naphtha*spiro*pyran gradually gives a blood-red solution, probably owing to formation of the potassium salt of the corresponding dinaphthylvinyl ketone. An examination of this question and a study of other similarly constituted *spiro*pyrans are now in progress.

Since the completion of this work a communication has appeared by Löwenbein and Katz (*Ber.*, 1926, **59**, 1377) dealing with the preparation of certain 2-aryl derivatives of (IV) obtained by the condensation of 2-naphthol-1-aldehyde with α-arylacetoacetic esters. These compounds also yield di-β-naphtha*spiro*pyrans analogous to (VII), all of which exhibit similar colour changes in high-boiling solvents. The conclusions arrived at by these authors to account for the phenomenon are wholly in harmony with the views expressed above.

Dilthey and Wizinger (*Ber.*, 1926, **59**, 1856) announce in a preliminary notice that they also have prepared di-β-naphtha*spiro*pyran, but no details of their method are available. These authors,

who have approached the problem from another direction, regard the coloured form as a dipolar anhydride (IX) of the normal *spiro*pyran.



(IX.)

EXPERIMENTAL.

1-Acetonyl-3-methyl-1 : 4-β-naphthapyran (II).—2-Naphthol-1-aldehyde (5 g.) (Fosse, *Bull. Soc. chim.*, 1901, 25, 371) was dissolved in a mixture of alcohol and acetone (20 c.c. of each) and treated with 50% potassium hydroxide (8 c.c.). The mixture was gently heated under reflux for 3 hours, and after cooling, the blood-red liquid was extracted with ether. The ethereal solution was washed, dried, and concentrated, whereupon a small quantity of a crystalline solid separated. The remainder of the extract consisted of an unworkable brown resin. After three recrystallisations from alcohol, the solid was obtained in faintly yellow, fern-like aggregates, m. p. 152—153°. The compound, which is insoluble in water and aqueous sodium hydroxide, gives no coloration with alcoholic hydrogen chloride and only slowly absorbs bromine, hydrogen bromide being evolved (Found: C, 80·6; H, 6·3. $C_{17}H_{16}O_2$ requires C, 80·95; H, 6·35%).

After removal of dissolved ether by a current of warm air, the blood-red aqueous liquid, on saturation with either carbon dioxide or dilute hydrochloric acid, deposited a yellow solid which, on drying, became dull olive-green. By repeated precipitation from benzene or ethyl acetate by addition of light petroleum, it was obtained as an amorphous, yellow powder, melting above 250° and insoluble in aqueous alkali.

Derivatives of 3-Styryl-β-naphthapyrylium Chloride.—These salts were all prepared by the same general method—saturation of an alcoholic solution of 2-naphthol-1-aldehyde and the requisite styryl methyl ketone with hydrogen chloride. The styryl ketone was always used in slight excess, in order to avoid the formation of di-β-naphthapyrylium chloride (Betti and Mundici, *Atti R. Accad. Lincei*, 1904, v, **13**, ii, 542; *Gazzetta*, 1905, **35**, ii, 46). It was found advantageous to condense small amounts of material at a time, otherwise the product either failed to separate or was only obtained in small yield. As is the case with the corresponding benzopyrylium chlorides, formic acid was found to be the best crystallising medium,

ether being added to reduce the solubility. No melting points are recorded for these salts, as on heating they gradually decompose and pass into tars.

3-*Styryl*-β-*naphthapyrylium chloride* was prepared as above from styryl methyl ketone (Knoevenagel, *Annalen*, 1914, **402**, 111) and 2-naphthol-1-aldehyde. The salt separated from formic acid, containing about 60% of anhydrous ether, in centimetre-long, thin plates which appeared blood-red in transmitted light and showed a pronounced beetle-green reflex. It is moderately easily soluble in water to an orange-yellow solution, readily so in alcohol or acetone to a deep orange liquid; in concentrated sulphuric acid the colour is orange-red. All the solutions have an intense greenish-yellow fluorescence (Found: C, 72·5; H, 4·9; Cl, 9·6. $C_{21}H_{15}OCl,HCO_2H$ requires C, 72·4; H, 4·7; Cl, 9·7%).*

3-p-*Hydroxystyryl*-β-*naphthapyrylium chloride*, prepared from *p*-hydroxystyryl methyl ketone (Buck and Heilbron, J., 1922, **121**, 1101), forms glistening, dark olive-green prisms, which are deep violet by transmitted light (under the microscope). The salt is slightly soluble in water to a cherry-red solution, which on dilution passes through violet to almost pure blue, the change being completed by addition of a drop of dilute sodium bicarbonate solution. The blue solutions slowly fade until they are almost colourless (10—15 minutes). With dilute aqueous sodium hydroxide, the blue colour persists for a few seconds only, after which a red colour, resembling that of the parent chloride, gradually develops. The salt dissolves in concentrated sulphuric acid to a reddish-orange liquid with an intense greenish-orange fluorescence (Found: C, 68·1; H, 4·6; Cl, 9·6. $C_{21}H_{15}O_2Cl,2H_2O$ requires C, 68·0; H, 5·1; Cl, 9·6%).

3-3′-*Methoxy*-4′-*hydroxystyryl*-β-*naphthapyrylium chloride*, prepared from 3-methoxy-4-hydroxystyryl methyl ketone (McGookin and Sinclair, J., 1926, 1578), forms aggregates of dull green needles, sparingly soluble in water to a pink solution. In alcohol the colour is bluish-purple, becoming purplish-red on addition of a little water. In its behaviour with water and alkalis it closely resembles the *p*-hydroxy-analogue. In concentrated sulphuric acid, it gives a red solution with a dark red fluorescence (Found: C, 65·8; H, 4·9; Cl, 8·9. $C_{22}H_{17}O_3Cl,2H_2O$ requires C, 65·9; H, 5·2; Cl, 8·9%).

3-p-*Methoxystyryl*-β-*naphthapyrylium chloride*, prepared from *p*-methoxystyryl methyl ketone (Baeyer and Villiger, *Ber.*, 1902, **35**, 1189), separates in prisms resembling the *p*-hydroxy-analogue but also showing a faint golden reflex. It is soluble in alcohol to a

* All halogen estimations were carried out by Stepanoff's method (*Ber.*, 1906, **39**, 4056) as modified by van Duin (*Rec. trav. chim.*, 1926, **45**, 343).

deep purplish-red solution with an intense red fluorescence, which disappears on addition of water. Its aqueous solution in high dilution is pink, which slowly fades to pale yellow, a slight opalescence being also present. In concentrated sulphuric acid, the solution is orange-red with a fluorescence similar to that of the *p*-hydroxy-compound (Found : C, 66·9 ; H, 5·2 ; Cl, 8·7. $C_{22}H_{17}O_2Cl,HCO_2H,H_2O$ requires C, 66·9 ; H, 5·1 ; Cl, 8·6%).

3-3′ : 4′-*Dimethoxystyryl*-β-*naphthapyrylium chloride*, prepared from 3 : 4-dimethoxystyryl methyl ketone (Kaufmann and Radosević, *Ber.*, 1916, **49**, 675), crystallises in dark green prisms with a bronze reflex. In its properties it closely resembles the *p*-methoxy-analogue, except that its alcoholic solution does not fluoresce and in concentrated sulphuric acid the fluorescence is very weak (Found : C, 65·1 ; H, 5·3 ; Cl, 7·8. $C_{23}H_{19}O_3Cl,HCO_2H,H_2O$ requires C, 65·1 ; H, 5·2 ; Cl, 8·0%).

3-3′ : 4′-*Methylenedioxystyryl*-β-*naphthapyrylium chloride* was obtained as a felted mass of minute, dark green needles (Found : C, 64·6 ; H, 4·5 ; Cl, 8·4. $C_{22}H_{15}O_3Cl,HCO_2H,H_2O$ requires C, 64·7 ; H, 4·5 ; Cl, 8·3%).

3-p-*Dimethylaminostyryl*-β-*naphthapyrylium Perchlorate*.—A solution of *p*-dimethylaminostyryl methyl ketone (2·1 g.) and 2-naphthol-1-aldehyde (2 g.) in glacial acetic acid (20 c.c.) was saturated with dry hydrogen chloride, acetic acid (10 c.c.) and 60% perchloric acid (5 c.c.) were added, and the whole was kept over-night. The separated solid, after being washed with acetic acid and with ether, consisted of small, chocolate-brown needles with a steely blue reflex. On treatment with acetone, a minute amount dissolved, giving a bright green solution ; the residue was converted into a mass of emerald-green needles. Both crystalline forms are very sparingly soluble in alcohol to greenish-blue solutions, which with water change to pure azure blue. The brown crystals probably contain some addendum, for on keeping over solid potassium hydroxide in an exsiccator they slowly become dark green. Neither form has been analysed, owing to the explosive character of the compound.

3-(β-2′-*Hydroxy*-1′-*naphthylvinyl*)-β-*naphthapyrylium Chloride* (IV).—A solution of 2-naphthol-1-aldehyde (5 g.) in alcohol (75 c.c.) and acetone (10 c.c.) was saturated with hydrogen chloride. The liquid, at first deep indigo-blue, finally exhibited pleochroism, being brownish-red in thick and olive-green in thin layers. After 12 hours, the crystalline deposit was collected and recrystallised in the usual way, being obtained as a felted mass of small, dark green needles. It is insoluble in water, and moderately easily soluble in alcohol to an indigo-blue solution. Hot water rapidly hydrolyses the compound to the *spiro*pyran. On keeping over solid potassium hydr-

oxide, a continuous slow loss of hydrogen chloride takes place; the substance loses its crystalline form and is converted into a dirty, purplish-coloured, amorphous mass, which contains a small amount of chlorine even after 3 months' keeping in a vacuum. Analysis of the salt was carried out immediately the compound had lost all odour of formic acid (Found: C, 69·2; H, 5·1; Cl, 8·0. $C_{25}H_{17}O_2Cl,HCO_2H,H_2O$ requires C, 69·6; H, 4·7; Cl, 7·9%).

Di-β-*naphtha*spiro*pyran* (VII) was prepared from the foregoing pyrylium salt by two methods. (i) The salt was dissolved in alcohol, and water added to the warm solution. (ii) The chloride was heated with water and treated with sodium acetate to ensure complete hydrolysis. The resultant pale blue solid was twice recrystallised from xylene, separating in colourless, irregular, thin plates, with a pearly lustre, which darkened at 240° and became tarry at about 260°. The spiro*pyran* is insoluble in water, and only sparingly soluble in the usual low-boiling solvents. It is soluble in warm, high-boiling liquids such as xylene, phenetole, nitrobenzene, and naphthalene. When it is heated with such a solvent, a purple colour develops at about 100°, becoming progressively darker as the temperature rises. In phenol or glacial acetic acid, the solution is intensely coloured in the cold. Suspended in alcohol and treated with hydrogen chloride, the *spiro*pyran reverts to the original pyrylium salt. When it is boiled with aqueous-alcoholic sodium hydroxide, a pink colour develops, which changes to blood-red after several hours' refluxing. The carmine solution in concentrated sulphuric acid shows a dark red fluorescence (Found: C, 85·8; H, 4·7; *M*, ebullioscopic in nitrobenzene, 344, 352, 334. $C_{25}H_{16}O_2$ requires C, 86·2; H, 4·6%; *M*, 348).

We desire to record our thanks to the Council of the Department of Scientific and Industrial Research for a grant to one of us (R. D.) which enabled this research to be carried out.

THE UNIVERSITY, LIVERPOOL. [*Received, October 27th,* 1926.]

III.—3-*Nitro*-4-*amino*- *and the* 3 : 4-*Dihalogenobenzaldehydes.*

By HERBERT HENRY HODGSON and HERBERT GREENSMITH BEARD.

THE substituted benzaldehydes described in this paper were required for an investigation of the colour and constitution of dyes of the triphenylmethane series. They were all prepared at first from 3-nitro-4-aminobenzaldehyde; later, however, by a modification

of Erdmann's method (D.R.-P. 62180), the 4-halogeno-3-nitrobenzaldehydes were obtained from the 4-halogenobenzaldehydes by direct nitration.

The preparation of a mononitro-derivative of *p*-aminobenzaldehyde was patented by Kalle and Co. (D.R.-P. 89244), but Walther and Bretschneider (*J. pr. Chem.*, 1898, **57**, 535) were unable to reproduce their result. Cohn and Springer (*Monatsh.*, 1903, **24**, 87) obtained 3-nitro-4-acetamidobenzaldehyde by nitrating *p*-acetamidobenzaldehyde with a mixture of sulphuric and nitric acids, and converted it into 3-nitro-4-aminobenzaldehyde by hydrolysing it with concentrated hydrochloric acid. This method, however, gave in our hands a very poor yield of a mixture of products, and the nitration of *p*-acetamidobenzaldehyde was much improved by using diacetylorthonitric acid in acetic anhydride solution; in this case formation of *p*-acetamidobenzylidene diacetate preceded nitration. The acetate groups can be removed from 3-nitro-4-acetamidobenzylidene diacetate either separately or together.

The various melting points recorded by Cohn and Springer (*loc. cit.*) have been confirmed, and the constitutions of all the aldehydes described in this paper have been established by converting them into the corresponding benzoic acids by oxidation with neutral aqueous permanganate.

The yellow *leuco*-compound obtained by condensing 3-nitro-4-aminobenzaldehyde with diethylaniline in hydrochloric acid solution gives, on oxidation, a dye which imparts to wool a blue shade with a faint red tint. Since benzaldehyde, similarly treated, gives a brilliant green dye, the influence of substitution in the condensing aldehyde on the colour of the triphenylmethane dye appears to be pronounced and is being investigated.

EXPERIMENTAL.

3-*Nitro*-4-*aminobenzaldehyde*.

The initial material, *p*-aminobenzaldehyde, was prepared by Geigy's process (D.R.-P. 86874) from *p*-nitrotoluene (300 g.) and sodium disulphide in boiling alcohol. Three-quarters of the alcohol were recovered prior to steam distillation, which removed most (120 g.) of the *p*-toluidine simultaneously formed; the non-volatile *p*-aminobenzaldehyde was then extracted with ether.

The crude product was directly acetylated by suspension in water (200 c.c.) and treatment first with glacial acetic acid (200 c.c.), a red precipitate forming, and then gradually with acetic anhydride (160 c.c.); the reaction was completed by heating on the water-

bath until the solid dissolved (30 min.). On pouring the mixture into ice-water (1500 c.c.) a yellow, crystalline solid separated, and more was obtained by making the filtrate just alkaline and adding sodium chloride. The total yield was 145 g. of a mixture of *p*-acetamidobenzaldehyde, aceto-*p*-toluidide, and a small quantity of *p*-aminobenzylidene-*p*-toluidine.

This mixture (135 g.) was heated slowly to 50° with 33% aqueous sodium bisulphite (400 c.c.) and water (200 c.c.) and cooled, the undissolved portion was well washed, and the combined filtrate and washings were treated with 20% aqueous sodium hydroxide as long as *p*-acetamidobenzaldehyde was precipitated. This substance was colourless when freshly prepared but became more and more yellow on keeping. It crystallised from water in prisms, m. p. 156° (Janse, *Rec. trav. chim.*, 1921, **40**, 285, gives m. p. 152°) (Found: N, 8·7. Calc.: N, 8·6%). The p-*nitrophenylhydrazone* separated from alcohol in deep orange needles, m. p. 264—265° (Found: N, 19·0. $C_{15}H_{14}O_3N_4$ requires N, 18·8%).

The insoluble portion of the above mixture, on fractional crystallisation from alcohol, gave p-*acetamidobenzylidene*-p-*toluidine* as the least soluble constituent; this was identified by comparison with a specimen, m. p. 187—188°, prepared from *p*-toluidine and *p*-acetamidobenzaldehyde (Found: N, 11·2. $C_{16}H_{16}ON_2$ requires N, 11·1%).

During the above operations, partial change of the *p*-aminobenzaldehyde into its amorphous, insoluble modification occurred, and this could only be acetylated by warming with acetic anhydride.

Nitration of p-*Acetamidobenzaldehyde.*—The aldehyde (30 g.) was obtained in small crystals by rapidly cooling a warm solution in acetic anhydride (75 c.c.) to 20°. Diacetylorthonitric acid (40 c.c.) was gradually added, the temperature not being allowed to exceed 40—50°. The crystals dissolved; after the addition of about 12 c.c. of diacetylorthonitric acid colourless plates of *p*-acetamidobenzylidene diacetate separated; these dissolved on further addition of the acid and remained in solution even on cooling. Nitration had not yet occurred, and numerous experiments have indicated the preliminary formation of this diacetate to be essential to smooth nitration. After the diacetylnitric acid had been added, the mixture was kept at 50° for 15 minutes, cooled, and poured into ice-water (400 c.c.) with vigorous stirring. After 2 hours, the 3-*nitro*-4-*acetamidobenzylidene diacetate* produced was filtered off, washed, and dried (yield, 45 g.). It gave no hydrazone and crystallised from alcohol in pale yellow leaflets, m. p. 114° (Found: N, 8·7. $C_{13}H_{14}O_7N_2$ requires N, 9·0%). It was easily soluble in alcohol or glacial acetic acid but sparingly soluble in chloroform.

Unlike *p*-acetamidobenzaldehyde, *p*-acetamidobenzylidene diacetate remains unchanged in colour on keeping. It melts at 170° (Blanksma, *Chem. Weekblad*, 1909, 6, 899, gives m. p. 166°) (Found : N, 5·5. Calc. : N, 5·3%).

Hydrolysis of 3-Nitro-4-acetamidobenzylidene Diacetate.—The diacetate (10 g.) was heated on the water-bath for 15 minutes with concentrated hydrochloric acid (25 c.c.). Separation of *3-nitro-4-aminobenzaldehyde* from the cherry-coloured solution then began and was completed by the addition of water. The product was only slightly soluble in concentrated or dilute hydrochloric acid, cold alcohol, or glacial acetic acid; it deepened in colour from yellow through orange to old-gold on prolonged contact with hot hydrochloric acid, and crystallised from alcohol or water in orange needles, m. p. 191° (Cohn and Springer, *loc. cit.*, give m. p. 190·5—191°) (Found : N, 17·0. Calc. : N, 16·9%).

3-Nitro-4-acetamidobenzaldehyde was obtained when the diacetate (2 g.) was triturated with concentrated hydrochloric acid (10 c.c.) and the mixture was heated gradually to 40° until solution occurred, and then cooled rapidly and thrown into cold water (yield, 1·3 g.). It crystallised from hot water in pale yellow needles, m. p. 155° (Cohn and Springer, *loc. cit.*, give m. p. 155°) (Found : N, 12·9. Calc. : N, 13·4%). The p-*nitrophenylhydrazone* crystallises from alcohol in deep orange needles, m. p. 289—290° (Found : N, 20·6. $C_{15}H_{13}O_5N_5$ requires N, 20·5%).

3-Nitro-4-aminobenzaldehyde-p-*nitrophenylhydrazone* crystallises from glacial acetic acid in dark maroon needles, m. p. 270—272° (Found : N, 23·1. $C_{13}H_{11}O_4N_5$ requires N, 23·3%).

3-Nitro-4-aminobenzaldoxime crystallises from dilute alcohol in orange needles, m. p. 207°, and gives a deep red solution in aqueous sodium hydroxide (Found : N, 23·05. $C_7H_7O_3N_3$ requires N, 23·2%).

3-Nitrobenzaldehyde-4-azo-β-naphthol crystallises from glacial acetic acid in fine, crimson needles, m. p. 271° (Found : N, 13·2. $C_{17}H_{11}O_4N_3$ requires N, 13·6%). It is very slightly soluble in all the usual solvents and gives an insoluble, brick-red sodium salt.

Diazotisation of 3-Nitro-4-aminobenzaldehyde.—A solution of the aldehyde (4 g.) in warm 80% acetic acid (30 c.c.) was cooled, and to the paste of fine crystals thus obtained 20% aqueous sodium nitrite (10 c.c.) was added, followed gradually by concentrated hydrochloric acid (10 c.c.), the temperature being kept just below 20°. (Diazotisation takes place more readily at *ca.* 20° than at 0°, and without loss of nitrogen.) After the excess of nitrous acid had been destroyed by carbamide, the 4-halogeno-3-nitrobenzaldehydes were obtained by the usual Sandmeyer processes. The

4-chloro-compound could be obtained only in about 30% yield, probably owing to the formation of a diphenyl derivative, but 4-bromo- and 4-iodo-3-nitrobenzaldehydes were isolated in nearly quantitative amounts and almost pure.

The p-*Nitrophenylhydrazones of the* 4-*Halogeno*-3-*nitro- and* 3 : 4-*Dihalogeno-benzaldehydes.*

The *p*-nitrophenylhydrazones of the 4-halogeno-3-nitrobenzaldehydes are very sparingly soluble in the usual solvents and the conditions for their preparation described below must be carefully observed if they are to be obtained crystalline. When heated, they exhibit a colour change from orange to red at *ca.* 160° which is not reversed on cooling (compare Chattaway and Walker, J., 1924, **125**, 1210). The *p*-nitrophenylhydrazones of the 3 : 4-dihalogenobenzaldehydes are much more soluble.

A solution of the aldehyde (0·1 g.) in cold alcohol (5 c.c.) is made faintly turbid by dilution with water and is then heated to boiling, and a solution of *p*-nitrophenylhydrazine (0·6 g.) in alcohol (3 c.c.) and glacial acetic acid (0·5 c.c.) at the same temperature is added. The crystalline product that separates immediately has a very sharp m. p. When the method of preparation described by Hodgson and Beard (J., 1925, **127**, 880) is used, the product is non-crystalline and very sparingly soluble and has an indefinite m. p.

The 4-*Halogeno*-3-*nitrobenzaldehydes.*

4-Chloro-3-nitrobenzaldehyde forms colourless needles, m. p. 64·5°, from dilute alcohol (Erdmann, *loc. cit.*, gives m. p. 64·5°) (Found: Cl, 18·9. Calc.: Cl, 19·1%). The p-*nitrophenylhydrazone* forms orange needles, m. p. 278—279° (Found: Cl, 11·1. $C_{13}H_9O_4N_4Cl$ requires Cl, 11·1%) and the *oxime* crystallises from alcohol in pale yellow needles, m. p. 146° (Found: Cl, 17·6. $C_7H_5O_3N_2Cl$ requires Cl, 17·7%).

4-Chloro-3-nitrobenzoic acid crystallises from dilute acetic acid in colourless prisms, m. p. 180—181° (Hübner, *Z. Chem.*, 1866, **6**, 5, gives m. p. 178—180°) (Found: Cl, 17·5. Calc.: Cl, 17·6%).

4-Bromo-3-nitrobenzaldehyde separates from alcohol in pale yellow needles, m. p. 106° (Schöpff, *Ber.*, 1891, **24**, 3775, gives m. p. 103°) (Found: Br, 33·8. Calc.: Br, 34·0%), and is very volatile in steam. The p-*nitrophenylhydrazone* forms yellow, micro-crystalline needles, m. p. 282—283° (Found: Br, 21·8. $C_{13}H_9O_4N_4Br$ requires Br, 21·9%), and the oxime crystallises from dilute alcohol in orange needles, m. p. 154° (Schöpff, *loc. cit.*, gives m. p. 145—146°) (Found: Br, 32·3. Calc.: Br, 32·5%).

4-Bromo-3-nitrobenzoic acid crystallises from dilute acetic acid

in colourless, fern-like masses, m. p. 203° (Hübner, Philipp, and Ohly, *Annalen*, 1867, **143**, 248, give m. p. 199°) (Found : Br, 32·3. Calc. : Br, 32·5%).

4-*Iodo*-3-*nitrobenzaldehyde* is only very slowly volatile in steam. It is sparingly soluble in cold alcohol and crystallises from a hot solution in deep yellow needles, m. p. 141° (Found : I, 45·4. $C_7H_4O_3NI$ requires I, 45·8%). The p-*nitrophenylhydrazone* forms yellow, microcrystalline needles, m. p. 277—278° (decomp.) (Found : I, 30·5. $C_{13}H_9O_4N_4I$ requires I, 30·8%). The *oxime* forms pale yellow needles, m. p. 157°, from alcohol (Found : I, 43·5. $C_7H_5O_3N_2I$ requires I, 43·5%).

4-Iodo-3-nitrobenzoic acid crystallises from alcohol in yellow prisms, m. p. 213° (Glassner, *Ber.*, 1875, **8**, 562, gives m. p. 210°) (Found : I, 43·0. Calc. : I, 43·3%).

Preparation of the 4-*Halogeno*-3-*nitrobenzaldehydes by Direct Nitration of the* 4-*Halogenobenzaldehydes*.—The aldehyde (10 g.) is added gradually to a mixture of sodium nitrate (5·5 g.) and concentrated sulphuric acid (60 g.) kept at 15—20°, and the whole is then heated at 70° for 15 minutes, cooled, and poured on to ice; the yield is almost quantitative (compare Erdmann, *loc. cit.*).

The 3 : 4-*Dihalogenobenzaldehydes*.

These aldehydes were prepared from the 4-halogeno-3-nitrobenzaldehydes by the method already described (*J. Soc. Chem. Ind.*, 1926, **45**, 91T).

3 : 4-Dichlorobenzaldehyde crystallises from alcohol in colourless needles, m. p. 44° (Erdmann and Schwechten, *Annalen*, 1890, **260**, 72, give m. p. 44°) (Found : Cl, 40·3. Calc. : Cl, 40·5%). The p-*nitrophenylhydrazone* forms orange needles, m. p. 276—277° (Found : Cl, 22·7. $C_{13}H_9O_2N_3Cl_2$ requires Cl, 22·9%), and the *oxime* colourless needles, m. p. 118—119°, from dilute alcohol (E. and S., *loc. cit.*, give m. p. 114—115°) (Found : Cl, 37·1. Calc. : Cl, 37·3%).

3 : 4-Dichlorobenzoic acid crystallises from dilute acetic acid in colourless plates, m. p. 201—202° (Beilstein and Kuhlberg, *Annalen*, 1869, **152**, 232, give m. p. 201—202°) (Found : Cl, 36·9. Calc. : Cl, 37·1%).

4-*Chloro*-3-*bromobenzaldehyde* forms colourless needles, m. p. 70°, from alcohol (0·1460 g.; 0·2232 g.; 0·2210 g.*). The p-*nitrophenylhydrazone* forms orange needles, m. p. 273—274° (Found : N, 12·0. $C_{13}H_9O_2N_3ClBr$ requires N, 11·8%), and the *oxime*

* In this and in the other cases given later, the three quantities are, respectively, the weight of substance taken for analysis and the weights of mixed silver halides found and calculated.

crystallises from dilute alcohol in colourless needles, m. p. 131° (Found : N, 5·8. $C_7H_5ONClBr$ requires N, 5·5%).

4-Chloro-3-bromobenzoic acid separates from dilute acetic acid in colourless plates, m. p. 215—216° (Cohen and Raper, J., 1904, **85**, 1269, give m. p. 214°) (0·1180 g.; 0·1650 g.; 0·1657 g.).

4-*Chloro*-3-*iodobenzaldehyde* is very volatile in steam and separates from alcohol in colourless, spear-shaped crystals, m. p. 117° (0·1332 g.; 0·1846 g.; 0·1892 g.). The p-*nitrophenylhydrazone* forms orange needles, m. p. 277—278° (decomp.) (Found : N, 10·6. $C_{13}H_9O_2N_3ClI$ requires N, 10·5%), and the *oxime* is obtained from dilute alcohol in colourless needles, m. p. 115—116° (Found : N, 5·1. C_7H_5ONClI requires N, 5·0%).

4-*Chloro*-3-*iodobenzoic acid* separates from dilute acetic acid in colourless plates, m. p. 216—217° (0·1412 g.; 0·1872 g.; 0·1892 g.).

3-*Chloro*-4-*bromobenzaldehyde* crystallises from alcohol in colourless needles, m. p. 52° (0·1098 g.; 0·1150 g.; 0·1157 g.). The p-*nitrophenylhydrazone* separates in orange needles, m. p. 272—273° (Found : N, 12·1. $C_{13}H_9O_2N_3ClBr$ requires N, 11·8%), and the *oxime* in colourless needles, m. p. 104°, from dilute alcohol (Found : N, 5·7. $C_7H_5ONClBr$ requires N, 5·5%).

3-Chloro-4-bromobenzoic acid crystallises from dilute acetic acid in colourless plates, m. p. 219° (Cohen and Raper, J., 1904, **85**, 1262, give m. p. 218°) (0·1180 g.; 0·1652 g.; 0·1657 g.).

3 : 4-*Dibromobenzaldehyde* separates from alcohol in colourless needles, m. p. 75° (Found : Br, 60·7. $C_7H_4OBr_2$ requires Br, 60·6%). The p-*nitrophenylhydrazone* separates in orange needles, m. p. 270—274° (Found : Br, 39·9. $C_{13}H_9O_2N_3Br_2$ requires Br, 40·2%), and the *oxime* in colourless needles, m. p. 129°, from dilute alcohol (Found : Br, 57·1. $C_7H_5ONBr_2$ requires Br, 57·3%).

3 : 4-Dibromobenzoic acid crystallises from dilute acetic acid in colourless plates, m. p. 233—234° (Hübner, *Annalen*, 1884, **222**, 184, gives m. p. 232—235°) (Found : Br, 50·4. Calc. : Br, 50·7%).

4-*Bromo*-3-*iodobenzaldehyde* is obtained from alcohol in thick, colourless prisms, m. p. 127° (0·1555 g.; 0·2134 g.; 0·2115 g.). The p-*nitrophenylhydrazone* forms orange needles, m. p. 265° (decomp.) (Found : N, 9·5. $C_{13}H_9O_2N_3BrI$ requires N, 9·4%), and the *oxime* colourless needles, m. p. 141°, from dilute alcohol (Found : N, 4·6. C_7H_5ONBrI requires N, 4·3%).

4-*Bromo*-3-*iodobenzoic acid* crystallises from dilute acetic acid in colourless needles, m. p. 243—244° (0·1082 g.; 0·1052 g.; 0·1060 g.).

3-*Chloro*-4-*iodobenzaldehyde* is very volatile in steam and separates from glacial acetic acid in colourless needles, m. p. 70·5° (0·1066 g.; 0·1482 g.; 0·1515 g.). The p-*nitrophenylhydrazone* forms orange

needles, m. p. 261—262° (decomp.), from dilute alcohol (Found: N, 10·7. $C_{13}H_9O_2N_3ClI$ requires N, 10·5%), and the *oxime* colourless needles, m. p. 129°, from alcohol (Found: N, 5·3. C_7H_5ONClI requires N, 5·0%).

3-*Chloro*-4-*iodobenzoic acid* crystallises from glacial acetic acid in colourless plates, m. p. 219° (0·1412 g.; 0·1862 g.; 0·1892 g.).

3-*Bromo*-4-*iodobenzaldehyde* crystallises from alcohol in colourless needles, m. p. 66° (0·1550 g.; 0·2140 g.; 0·2115 g.). The *p-nitrophenylhydrazone* forms orange needles, m. p. 260—261° (decomp.), from dilute alcohol (Found: N, 9·6. $C_{13}H_9O_2N_3BrI$ requires N, 9·4%), and the *oxime* colourless needles, m. p. 157—158°, from alcohol (Found: N, 4·5. C_7H_5ONBrI requires N, 4·3%).

3-*Bromo*-4-*iodobenzoic acid* crystallises from glacial acetic acid in colourless plates, m. p. 242—243° (0·1630 g.; 0·2062 g.; 0·2115 g.).

3 : 4-*Di-iodobenzaldehyde* crystallises from alcohol in colourless, micro-crystalline needles, m. p. 118° (Found: I, 71·0. $C_7H_4OI_2$ requires I, 70·95%). The *p-nitrophenylhydrazone* forms orange needles, m. p. 245—247° (decomp.), from dilute alcohol (Found: I, 51·3. $C_{13}H_9O_2N_3I_2$ requires I, 51·6%), and the *oxime* colourless needles, m. p. 177—178°, from alcohol (Found: I, 68·2. $C_7H_5ONI_2$ requires I, 68·1%).

3 : 4-Di-iodobenzoic acid crystallises from glacial acetic acid in colourless plates, m. p. 256—258° (Wheeler and Liddle, *Amer. Chem. J.*, 1909, **42**, 444, give m. p. 257°) (Found: I, 67·7. Calc.: I, 67·9%).

The authors desire to thank the Department of Scientific and Industrial Research for a grant to one of them (H. G. B.), and Messrs. J. W. Leitch and Co. and the British Dyestuffs Corporation for gifts of chemicals.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, September 24th,* 1926.]

IV.—*Arylseleninic Acids.*

By WILLIAM HENRY PORRITT.

Two toueneseleninic acids have been recorded by Doughty and Elder (Eighth Inter. Congress Applied Chemistry, 1912, **6**, 93) as resulting from the reduction by hydrochloric acid of the mixed toueneselenonic acids obtained by the direct action of selenic acid on toluene. The *p*-substituted acid was described as containing $1H_2O$ and melting with decomposition at 160°, whereas the *o*-isomeride, with melting point 99—101°, was stated to contain $\frac{1}{2}H_2O$.

The *m*-seleninic acid and two xyleneseleninic acids not hitherto described and the foregoing *o*- and *p*-tolueneseleninic acids have now been obtained from definitely oriented aromatic derivatives.

A correction. The action of hydrogen peroxide on two arylselenoglycollic acids was stated by Morgan and Porritt (J., 1925, **127**, 1758) to give rise to the corresponding arylselenoxyglycollic acids. Mr. F. C. Ray, of Battersea Polytechnic, kindly notified the author that this statement is erroneous, and further investigation has shown that the oxidising action of the hydrogen peroxide is sufficiently violent to remove the $CH_2 \cdot CO_2H$ group and give the corresponding arylseleninic acids.

This oxidation process, which has been repeated and extended, affords a ready and general method for preparing arylseleninic acids containing substituents of known orientation. If the temperature is allowed to rise appreciably during the first stage of the reaction between hydrogen peroxide and the arylselenoglycollic acid, the formation of the arylseleninic acid is attended by the production of other oxidation products and diaryl diselenides also may be isolated. The tolueneseleninic acids as prepared by this general method are obtained in anhydrous forms.

Experimental.

o-*Tolylselenoglycollic acid*, $CH_3 \cdot C_6H_4 \cdot Se \cdot CH_2 \cdot CO_2H$, was prepared by the general method (Morgan and Porritt, *loc. cit.*, p. 1775) from magnesium *o*-tolyl bromide and selenium (Taboury, *Bull. Soc. chim.*, 1903, **29**, 761), the condensation of the potassium salt of the mercaptan with sodium chloroacetate being effected in aqueous solution. The *selenoglycollic acid* separated as an oil from an acidified solution of its sodium salt and solidified slowly; after repeated crystallisation from boiling water, it was obtained in colourless, lustrous plates, m. p. 70—71° (Found: C, 47·2; H, 4·5. $C_9H_{10}O_2Se$ requires C, 47·2; H, 4·4%). It developed a reddish-brown colour in concentrated sulphuric acid.

m-*Xylyl*-4-*selenoglycollic Acid*, $(CH_3)_2C_6H_3 \cdot Se \cdot CH_2 \cdot CO_2H$.—4-Iodo-*m*-xylene, prepared from *m*-4-xylidine, was converted by the general reaction into the *selenoglycollic acid*, which separated as an oil and subsequently crystallised in colourless, lustrous plates, m. p. 90·5° (Found: C, 49·5; H, 5·0. $C_{10}H_{12}O_2Se$ requires C, 49·4; H, 4·9%). The acid developed a greenish-yellow colour in sulphuric acid.

o-*Xylyl*-4-*selenoglycollic acid*, prepared by the general method from 4-iodo-*o*-xylene obtained from *o*-4-xylidine (m. p. 49°; Morgan and Hickinbottom, *J. Soc. Chem. Ind.*, 1926, **45**, 222T), crystallised from hot water in colourless plates, m. p. 88°, and developed a violet coloration in sulphuric acid (Found: C, 49·5; H, 5·1%).

Toluene-o-*seleninic acid*, $CH_3 \cdot C_6H_4 \cdot SeO_2H$, was prepared by adding an excess of 20% hydrogen peroxide to a suspension of *o*-tolylselenoglycollic acid in ice-cold water, the acid gradually dissolving. The product, which separated after several hours, crystallised from hot water in clusters of colourless needles, m. p. 126—127° (Found: C, 41·4; H, 4·0. $C_7H_8O_2Se$ requires C, 41·4; H, 3·9%). It dissolved sparingly in ether and more readily in alcohol or chloroform.

Toluene-p-*seleninic acid*, prepared from *p*-tolylselenoglycollic acid, crystallised from hot water in colourless, flattened needles, m. p. 171° (Found: C, 41·7; H, 4·3%). Like the preceding isomeride, it developed a violet coloration with warm concentrated sulphuric acid and liberated iodine from acidified solutions of potassium iodide.

Toluene-m-*seleninic acid*, prepared by the oxidation with hydrogen peroxide of oily *m*-tolylselenoglycollic acid obtained from 3-iodotoluene through the Taboury reaction, separated from hot water in colourless needles, m. p. 119—120° (Found: C, 41·5; H, 4·0%). It developed a deep blue coloration with warm sulphuric acid.

Bromobenzene-p-*seleninic acid*, $C_6H_4Br \cdot SeO_2H$, prepared from *p*-bromophenylselenoglycollic acid by oxidation with hydrogen peroxide in acetic acid solution, crystallised from hot water in colourless needles, decomp. 187° (Found: C, 27·4; H, 1·9. $C_6H_5O_2BrSe$ requires C, 26·9; H, 1·9%). The sulphuric acid coloration was reddish-purple.

m-*Xylene*-4-*seleninic acid*, $(CH_3)_2C_6H_3 \cdot SeO_2H$, prepared by the general method of oxidation from the corresponding selenoglycollic acid, crystallised from water in colourless needles, decomp. 146—147° (Found: C, 44·0; H, 4·5. $C_8H_{10}O_2Se$ requires C, 44·2; H, 4·6%).

o-*Xylene*-4-*seleninic acid* crystallised from hot water in colourless needles, decomp. 125° (Found: C, 44·4; H, 4·7%).

The two xyleneseleninic acids developed deep blue colorations with warm concentrated sulphuric acid.

Di-o-*tolyl selenide*, $Se(C_7H_7)_2$, was prepared by the action of selenium on magnesium *o*-tolyl bromide and isolated during the preparation of *o*-tolylselenoglycollic acid after extraction of the ethereal solution of the selenomagnesium bromide with aqueous caustic potash. By repeated crystallisation from absolute alcohol, it was obtained in flat, colourless, shining plates, m. p. 64° (Found: C, 64·5; H, 5·5. $C_{14}H_{14}Se$ requires C, 64·4; H, 5·4%).

UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

[*Received, November 11th*, 1926.]

V.—*Period of Induction in Chemical Reactions. Interaction of Mercuric Chloride and Sodium Hydrogen Carbonate.*

By Panchanan Neogi and Sukumar Neogi.

Whilst preparing certain compounds of mercury, the authors found that interaction between mercuric chloride and alkaline hydrogen carbonates does not take place at once, but that there is a distinct period of induction. The present paper deals with this particular reaction, and those with other salts are being investigated.

Standard solutions of mercuric chloride and sodium hydrogen carbonate were prepared. 10 C.c. of the sodium hydrogen carbonate solution were added as quickly as possible to 10 c.c. of the mercuric chloride solution in a 50 c.c. test-tube, which was then sharply shaken once; the interval between the moment of mixing and the first appearance of the red precipitate of oxychloride at the top of the mixture was read from a stop-watch. The moment when the last portion of the sodium hydrogen carbonate solution had been poured was taken as the moment of mixing. A lens was used to ascertain the moment when the precipitate first made its appearance at the lowest point of the meniscus, and a black background facilitated the observation. The concentrations of the reactants were varied severally and jointly, giving three sets of experiments: (1) constant concentration of mercuric chloride (Table I); (2) constant concentration of sodium hydrogen carbonate (Table II); and (3) variable concentrations of both mercuric chloride and sodium hydrogen carbonate (Tables III and IV).

The determination of the exact time when the precipitate just became detached from the lowest point of the meniscus required practice and sometimes six determinations were made with one particular mixture, the mean being taken.

Table I.

$C_{Hg} = 1{\cdot}467$; temp. 23°.

C_{Na}.	t.	$C_{Na} \times t = K$.
2·0000	31·5	63·00
1·6666	39·5	65·80
1·4228	45·5	64·97
1·2500	50·5	63·12
1·1110	55·5	61·60
1·0000	65·0	65·00
0·9090	72·0	65·44
0·8334	81·0	67·50
0·7692	85·0	65·38
0·7142	92·0	65·70
	Mean	64·76

Table II.

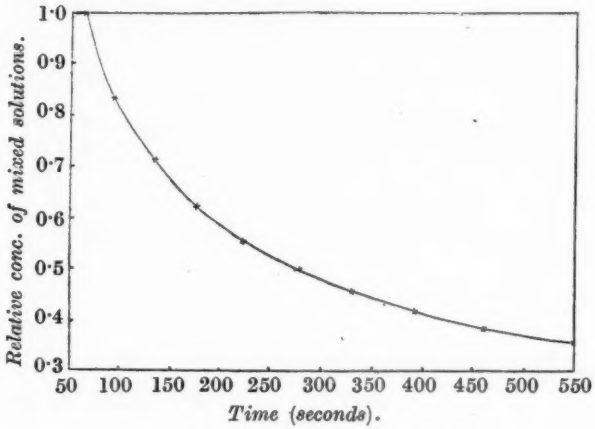
$C_{Na} = 1{\cdot}723$; temp. 23°.

C_{Hg}.	t.	$C_{Hg} \times t = K$.
1·476	41	60·51
1·2295	48	59·01
1·0548	58	61·17
0·9225	69	60·85
0·8144	78	63·95
0·7380	82	60·52
0·6708	87	58·34
0·6150	95	58·42
0·5676	102·5	58·00
0·5271	110·5	58·24
	Mean	59·90

C_{Hg} and C_{Na} represent concentrations of mercuric chloride and sodium hydrogen carbonate, respectively, in g.-mols. per 10 litres of water (10 c.c. of each solution were used in each experiment); t is the period of induction in seconds.

For the experiments in Tables III and IV, each reactant was diluted to 0·835, 0·71, 0·625, 0·55, 0·50, 0·45, 0·42, 0·38, and 0·36 of

FIG. 1.



its original concentration (see Fig. 1), but the values of C_{Na} in Table IV are double the corresponding values in Table III, the values of C_{Hg} remaining the same.

TABLE III.

Temp. 23°.

C_{Hg}.	C_{Na}.	t.	$C_{Na} . C_{Hg} . t = K$.
1·4760	1·000	65	95·94
1·2295	0·833	92	94·22
1·0547	0·7143	133	99·16
0·9225	0·625	175	100·89
0·8199	0·5555	221	100·65
0·7380	0·5000	270	99·63
0·6708	0·4545	330	104·61
0·6150	0·4167	392	104·69
0·5676	0·3846	460	100·43
0·5271	0·3571	550	103·52
		Mean	100·37

TABLE IV.

Temp. 23°.

C_{Na}.	t.	$C_{Na} . C_{Hg} . t = K$.
2·000	32	95·46
1·666	46	94·22
1·428	68	102·42
1·250	90	103·78
1·111	112	102·02
1·000	130	95·94
0·909	154	93·90
0·8334	190	97·49
0·7692	225	98·24
0·7143	250	96·63
	Mean	98·01

From Tables I—IV it will be seen that the period of induction is approximately inversely proportional to the concentration of the solutions. It was not possible to get more concordant results, as the reaction is apparently very complex (*vide infra*).

Effect of Temperature.

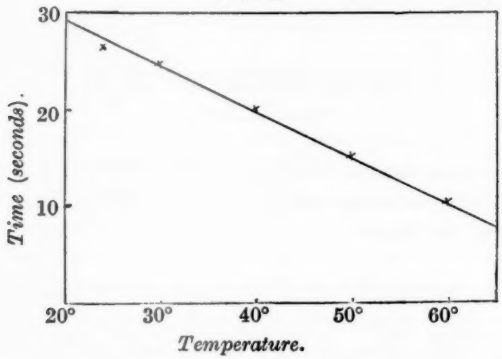
The two solutions contained in large test-tubes were kept in a glass thermostat for ½ hour, then the sodium hydrogen carbonate was immediately poured into the test-tube containing the mercuric chloride, and the period of induction read from the stop-watch. The experiment was repeated at 24°, 30°, 40°, 50°, and 60°, the concentrations of mercuric chloride and sodium hydrogen carbonate being kept constant. 10 C.c. of mercuric chloride ($C_{Hg} = 1{\cdot}476$) and 10 c.c. of sodium hydrogen carbonate ($C_{Na} = 2{\cdot}000$) were taken in each experiment.

TABLE V.

Temperature	24°	30°	40°	50°	60°
Period of induction (secs.) ...	31·5	26·1	20·0	15·0	10·5

The period of induction therefore diminishes, as the temperature is increased, approximately at the rate of 5 secs. for every increase of 10° (see Fig. 2).

FIG. 2.



The possible conversion of sodium hydrogen carbonate into carbonate when the temperature was raised was also studied; in addition to the two test-tubes containing mercuric chloride and sodium hydrogen carbonate, a third test-tube containing 10 c.c. of the same sodium hydrogen carbonate solution was suspended for ½ hour in the thermostat in each experiment under the same conditions of temperature. The conversion of hydrogen carbonate into carbonate was estimated with standard sulphuric acid solution by the double-indicator method :

Temperature	30°	40°	50°	60°
Carbonate formed ...	0·000598	0·000653	0·000761	0·010332

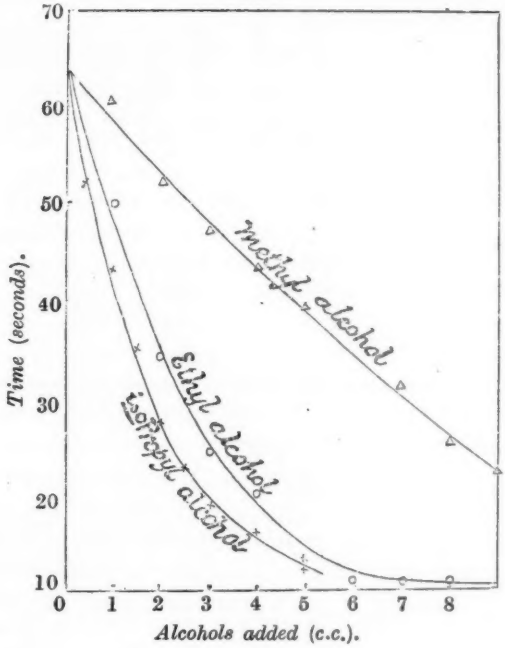
The proportion of carbonate in the hydrogen carbonate increases with the rise of temperature from 30° to 60°. Sodium hydrogen

carbonate solution (1 : 14) was found not to change during 24 hours at laboratory temperature.

Effect of Light.

Solutions of mercuric chloride ($C_{Hg} = 1{\cdot}476$) and sodium hydrogen carbonate ($C_{Na} = 2{\cdot}00$) were prepared in the dark-room and kept over-night. The period of induction, noted in red light on the following day, was found, after some trials in order to adjust vision in red light, to be the same as that in diffused daylight, *viz.*, 32 secs. at 22°. The reaction is therefore not photochemical.

FIG. 3.



Action of Alcohols.

The effect of alcohols and sugars on the period of induction was next studied. Methyl and ethyl alcohols progressively diminished the period of induction up to a certain limit. *iso*Propyl alcohol accelerated the reaction and hence diminished the period of induction, whereas *n*-propyl alcohol increased the period of induction so greatly that with 1·5 c.c. added to 20 c.c. of the mixture no precipitate was observed within ½ hour. In fact, *n*- and *iso*-propyl alcohols may be distinguished with the help of a dilute solution of mercuric chloride and sodium hydrogen carbonate. Glycerol caused a

pronounced increase in the period of induction, but glucose, sucrose, mannitol, and dulcitol had very little effect.

The concentrations of the two solutions were kept constant ($C_{Hg} = 1{\cdot}457$; $C_{Na} = 1{\cdot}000$); 10 c.c. of each solution were taken each time and the amount of alcohol added was increased, the alcohol being mixed with the mercuric chloride solution and the whole being cooled to 22° before the sodium hydrogen carbonate solution was added. The effects of methyl, ethyl, and *iso*propyl alcohols are plotted in Fig. 3.

Methyl alcohol (c.c.)	0	1	2	3	4	5	6	7	8	9	10
t (secs.)	67	62	52	47	43	39	37	31	25	22	20
Ethyl alcohol (c.c.)	0	1	2	3	4	5	6	7	8	9	
t (secs.)	63	50	34	24	20	15	12	11	11	11	
n-Propyl alcohol (c.c.)	0	0·2	0·4	0·6	0·8	1·0	1·5	2·0			
t (secs.)	63	108	132	143	160	1100	1200	1500			
*iso*Propyl alcohol (c.c.)	0	0·5	1·0	1·5	2·0	2·5	3·0	4·0	5·0		
t (secs.)	63	52	43	35	27·5	22·5	19	16	14		

Glycerol (c.c.)	0	1	2	3
t (secs.)	63	129	165	221

Wt. of substance added.	*t* (secs.).	Wt. of substance added.	*t* (secs.).
nil.	73*	0·0884 g. mannitol	74
0·4309 g. glucose	75	0·1235 „ „	75
0·2345 „ „	74	0·0775 „ dulcitol	75
0·2034 „ sucrose	74	0·0926 „ „	75·5
0·1245 „ „	74		

* This mixture was not of the same concentration as the foregoing.

Salts.

For obvious reasons, the effects of acids and alkalis could not be studied, but the action of certain salts, inorganic and organic, was investigated. 5 C.c. of an $M/10$-solution of a salt and 10 c.c. each of mercuric chloride and sodium hydrogen carbonate solutions were taken in each experiment, the temperature being 25°.

TABLE VI.

Substances added.	*t* (secs.).	Substances added.	*t* (secs.).
Water (5 c.c.)	28	Na Citrate	49
NaCl	68	K Citrate	48
KCl	67	Na Oxalate	54
Na_2SO_4	27	K Oxalate	54
K_2SO_4	27	$NaNO_3$	29
Na Tartrate	24	KNO_3	29
K Tartrate	24		

Table VI shows that chlorides, citrates, and oxalates markedly lengthen the period of induction, tartrates diminish it, and sulphates and nitrates have scarcely any action; further, that anions, but not

cations, influence the period of induction. This is quite in conformity with the work of Berczeller (*Int. Z. Biol.*, 1916, **2**, 444), who has shown that the effects of salts on the period of induction in the interaction of iodic and sulphurous acids are also dependent on the anions and not on the cations.

Discussion of Results.

The results given above establish the following points:

1. The period of induction is inversely proportional to the concentrations of each reactant, temperature being constant.
2. It diminishes with rise of temperature.
3. It increases with the addition of *n*-propyl alcohol, glycerol, chlorides, oxalates, and citrates, and diminishes with the addition of tartrates and of methyl, ethyl, and *iso*propyl alcohols. Nitrates, glucose, sucrose, mannitol, and dulcitol have no effect on the period of induction.

The present work agrees with Landolt's work on the action of sulphurous and iodic acids (*Ber.*, 1886, **19**, 1317) in that the period of induction in both cases is inversely proportional to the concentrations of the reactants.

The problem now is to determine the reactions which cause this period of induction. In the reaction between iodic and sulphurous acids, the separation of iodine is supposed to take place in several stages through iodous, hypoiodous, and hydriodic acids. In the case of mercuric chloride and sodium hydrogen carbonate, the intermediate reactions are obscure and complex. Under the conditions of our experiments, a red precipitate of the constitution $HgCl_2,2HgO$ is formed along with small quantities of the yellow oxychloride $HgCl_2,3HgO$. The black variety, $HgCl_2,2HgO$, is not formed until the red precipitate has been kept for some days. The formation of these oxychlorides has been reported by many workers, *e.g.*, Biltz (*Arch. Pharm.*, 1869, **190**, 202) and Thummel (*ibid.*, 1889, **27**, 589). It is evident that no carbonate is precipitated, and that carbon dioxide is evolved. Biltz thought that excess of sodium hydrogen carbonate formed a double salt, but Thummel has shown that the precipitate does not contain any mercuric carbonate, carbon dioxide being given off. We are of the opinion that the *formation of the oxychloride by the action of alkali hydrogen carbonate on mercuric chloride can never be instantaneous.* It would be more reasonable to suppose that mercuric carbonate or hydrogen carbonate is first formed and then combines with mercuric chloride in stages with the formation of oxychlorides and liberation of carbon dioxide. The work of previous workers shows that the two oxychlorides, $HgCl_2,2HgO$ (red) and $HgCl_2,3HgO$ (yellow), are precipitated, whilst

the unstable $2HgCl_2,HgO$ and $HgCl_2,HgO$ are probably formed as intermediate compounds, *e.g.*:

$$Hg(HCO_3)_2 + 2HgCl_2 = 2HgCl_2,HgO \text{ (unstable)} + 2CO_2 + H_2O;$$
$$2HgCl_2,HgO + Hg(HCO_3)_2 = 2HgCl_2,2HgO \text{ (unstable)} + 2CO_2 + H_2O.$$

Since the velocity of a reaction is proportional to the amount of the reacting substances, the speed of the formation of the red oxychloride is the result of the velocities of successive reactions such as those above, and the belated appearance of the red precipitate—the period of induction—corresponds with the time required for the consecutive reactions to take place before the actual precipitation of the red compound could commence. The fact that mercuric chloride is very feebly ionised in aqueous solution accounts for the smallness of the precipitate. That it has material influence on the period of induction also will be apparent from the following considerations:

(*a*) The slight ionisation of mercuric chloride in aqueous solution does not greatly increase with further dilution, and the number of ions present in solutions in which the concentration of mercuric chloride gradually diminishes therefore becomes less and less. As the velocity of ionic reactions depends on the concentration of the ions, it is evident that with further dilution the velocities of the intermediate reactions would be retarded, and hence the period of induction would increase.

(*b*) Arrhenius and others have shown that the ionisation of mercuric chloride increases in the presence of alcohols. This would explain the relatively large precipitate with alcoholic solutions of mercuric chloride and also the decrease in the period of induction in the case of methyl and ethyl alcohols, for, with increased ionisation, the velocities of the intermediate reactions would increase and hence the period of induction would decrease.

(*c*) Since rise of temperature also increases ionisation, the period of induction would decrease owing to the increased velocities of the intermediate reactions.

The action of methyl, ethyl, and *iso*propyl alcohols in shortening the period of induction may also be due to catalytic action. Their presence hastens the rates of the intermediate reactions, for it has been shown by Thummel (*Arch. Pharm.*, 1889), **27**, 589 that alcohols readily decompose the oxydichloride to the red dioxychloride. The catalytic effect of the alcohols in this case increases with their concentrations to a certain limit. Sodium chloride inhibits the reactions owing to the formation of double salts with mercuric chloride. The action of glycerol, nitrates, citrates, tartrates, and oxalates is probably catalytic in nature.

Conclusions.

1. A distinct period of induction precedes the precipitation of the red oxychloride in the interaction between mercuric chloride and sodium hydrogen carbonate.

2 The period of induction is inversely proportional to the concentration of each reactant, the temperature of the system being constant.

3. It diminishes as the temperature is raised, evidently owing to the increased velocities of intermediate reactions. It diminishes approximately at the rate of 5 seconds for a temperature increase of 10°.

4. The period of induction is the result of several successive reactions which take place before the final appearance of the red dioxychloride of mercury.

5. It diminishes with the addition of methyl, ethyl, or *iso*propyl alcohol or of tartrates, and increases with the addition of glycerol, *n*-propyl alcohol, chlorides, citrates, and oxalates. Sugars, such as glucose and sucrose, and polyhydric alcohols, such as mannitol and dulcitol, as well as nitrates and sulphates have scarcely any effect on the period of induction. The period of induction is influenced by the anions of salts and not by the cations.

6. The reaction is not photochemical in nature.

7. The feeble ionisation of mercuric chloride in aqueous solution explains the small quantity of precipitate produced. It has material influence on the period of induction also, since, owing to the low concentrations of ions on further dilution, the velocities of the intermediate reactions would be lessened and therefore the period of induction would increase. The reverse result is obtained when the ionisation of mercuric chloride is increased by the presence of methyl and ethyl alcohols or by raising the temperature.

8. A very dilute solution of mercuric chloride and sodium hydrogen carbonate may be used to distinguish between *n*- and *iso*-propyl alcohols: with the latter the precipitate of the red oxychloride appears within a few seconds, whilst with the normal alcohol the precipitation takes much longer—even more than ½ hour.

PRESIDENCY COLLEGE, CALCUTTA. [*Received, May 3rd,* 1926.]

VI.—*The Propagation of Flame in Mixtures of Methane and Air. Part V. The Movement of the Medium in which the Flame Travels.*

By WILLIAM RONALD CHAPMAN and RICHARD VERNON WHEELER.

PART IV of this research (J., 1926, 2139) described the determination of the conditions under which the flame travelling along a tube in a mixture of methane and air, initially quiescent and at atmospheric temperature and pressure, acquired its maximum speed. When the tube was 2—3 m. in length and 5 cm. in diameter, the conditions were that both ends should be open (ignition of the mixture being at one end) and that a number of restricting rings, reducing the diameter of the tube to one-half, should be introduced close together a short distance (50—100 cm.) from the point of ignition. Under these conditions, a speed as high as 420 m./sec. was obtained beyond the restrictions, the highest speed in an unrestricted tube of the same dimensions being about 6 m./sec.

It was shown that, during the propagation of flame in a tube open at both ends, the unburnt mixture in advance of the flame-front travels as a current in the same direction, and the flame is therefore moving in a medium which is itself in motion. The flame-speed at any point in the tube thus depends largely on the speed acquired by the medium, and the effect of restrictions is explained as being mainly an effect on the movement of the medium.

We have continued the study of the propagation of flame under different conditions in tubes restricted at certain points so as to control the movement of the unburnt mixture ahead of the flame. In this manner, we hoped to gain further information regarding the extent to which the movement of the flame depends on that of the medium in which it travels. All the experiments were made with a mixture of methane and air containing 9·5—10·0% of methane, using the brass tube, 5 cm. in diameter and 240 cm. long, previously described. The behaviour of the flame was studied by photographing it through a quartz lens on a rapidly revolving film as it passed a quartz window, 40 cm. long and 4 mm. wide, which could be placed in any desired position along the tube.

We have attempted to explain all the following results on the assumption that, under all conditions, there is a movement of the unburnt mixture ahead of the flame caused by the expansive force of the burning gases.

(A) *Ignition at One End of a Horizontal Tube Open at Both Ends.*

It has been recorded that when the tube is fully open at both ends the speed of the flame increases regularly over the first 80 cm. and is then slightly retarded (undulations making their appearance) to increase again after this temporary check. The initial acceleration of the flame is assumed to be due to the increasing speed with which the unburnt mixture is caused to move under the expansion of the burning gases. The acceleration would no doubt continue regularly throughout the length of a sufficiently short tube, but, in such a long tube as that used, cooling and condensation of the products of combustion cause a fall in pressure behind the flame which reduces the rate of acceleration of the unburnt mixture. As the flame travels further from the open end, the deficiency of pressure due to cooling and condensation being then less readily rectified by communication with the external atmosphere, the unburnt mixture, and therefore the flame, is retarded.

(a) *The Influence of a Restriction at the Ignition End of the Tube.*—The mean speeds of the flame over successive intervals when the end of the tube at which ignition was effected was reduced in diameter to 1·5 cm. are recorded in Table I. The speeds when the tube was fully open at both ends (see Part IV, Table I) are given for comparison. Similar, but less marked, results were obtained when the diameter of the tube at the ignition end was reduced to 2·5 cm.

Fig. 1, Plate I, is a composite photograph,* obtained in the manner described in Part IV, illustrating the manner in which the flame travels in a 9·75% methane–air mixture. This photograph should be compared with Fig. 1, Plate I, of Part IV.

TABLE I.

The Effect of Restricting the Ignition End of a Tube Open at Both Ends.

Distances from point of ignition (cm.).	Mean speed of flame (cm./sec.). Tube fully open at both ends.	Mean speed of flame (cm./sec.). Diam. at ignition end reduced to 1·5 cm.	Distances from point of ignition (cm.).	Mean speed of flame (cm./sec.). Tube fully open at both ends.	Mean speed of flame (cm./sec.). Diam. at ignition end reduced to 1·5 cm.
5—15	106	192	85— 95	249	827
15—25	134	220	95—125	229	1034
25—35	152	260	125—135	285	900
35—65	194	412	135—145	350	791
65—75	240	618	145—175	441	1016
75—85	254	721	175—205	575	1800

* This photograph is reduced to about $\frac{1}{5}$th of the size of the original; allowing for this, the speed of travel of the film can be regarded as 11·5 cm./sec.

The partial closure of the ignition end impedes the release of pressure at that end, so that a greater and more prolonged pressure is available to propel the column of unburnt mixture ahead of the flame. The speed of the flame is thus more rapidly accelerated than when the ignition end of the tube is fully open, and a further distance is travelled (125 cm. as compared with 80 cm.) before the influence of cooling behind the flame causes a retardation. This retardation is, however, greater in the former case, there being a 25% as compared with a 10% reduction in speed, because communication with the outside air is restricted.

(b) *The Influence of a Restriction at the Ignition End of the Tube together with Restrictions in the Path of the Flame.*—When the end of the tube at which the mixture was ignited was partly closed and one or more restricting rings were introduced at intervals along the tube, the speed of the flame during its passage depended upon the amount of restriction at each point, except that reduction of the diameter of the tube at the ignition end to 1·5 cm. or less was no more effective than reduction to 2·5 cm. Indeed, when there were two or three restrictions in the tube, the maximum effect on the speed of the flame was obtained when the diameter at the ignition end was 2·5 cm., whilst, as recorded in Part IV, when there were several restrictions close together, the maximum effect was obtained with both ends of the tube fully open.

The mean speeds of the flame before and after passing one restricting ring, 110 cm. from the ignition end of the tube, the diameter of which was reduced to 2·5 cm., are recorded in Table II.

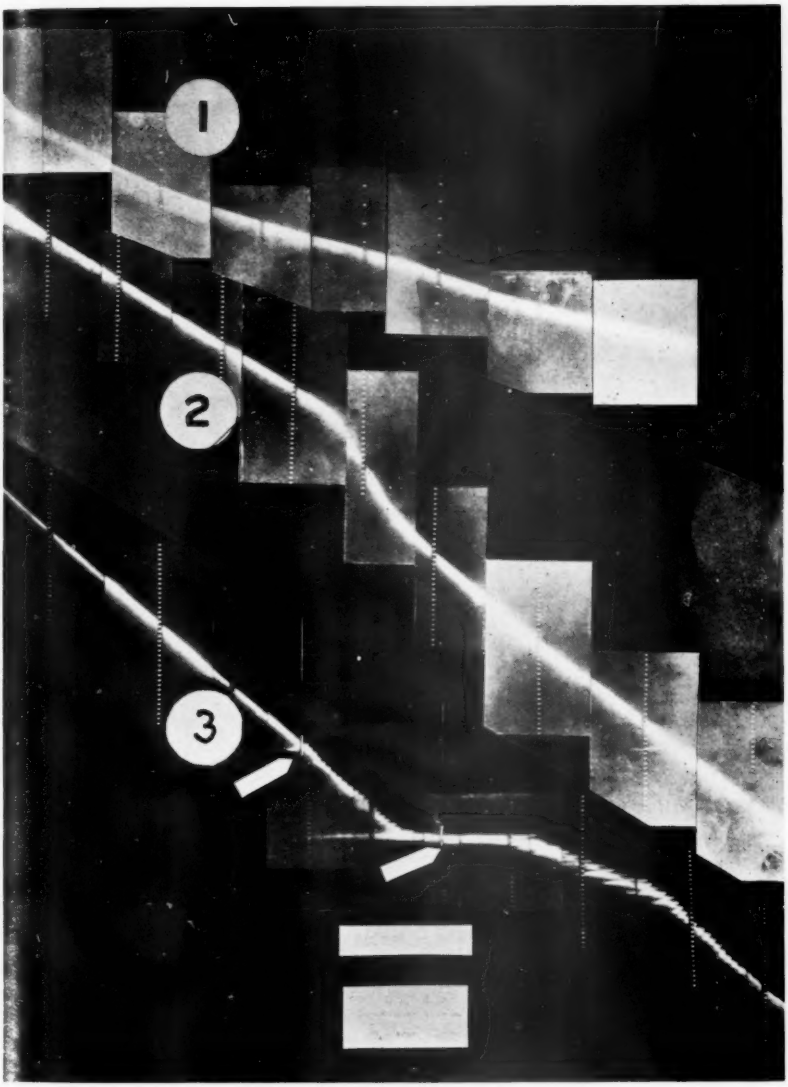
TABLE II.

The Effect of One Restriction in a Tube with Restricted Ignition End.

Distance from point of ignition (cm.).	Mean speed of flame (cm./sec.). Aperture in restriction 2·5 cm. diam.	Aperture in restriction 1·0 cm. diam.	Distance from point of ignition (cm.).	Mean speed of flame (cm./sec.). Aperture in restriction 2·5 cm. diam.	Aperture in restriction 1·0 cm. diam.
75— 85	256	95	135—145	1766	5,077
85— 95	289	84	145—155	1527	6,455
95—105	307	83	155—165	1319	7,833
105—115	Restriction at 110.	Restriction at 110.	165—175	1424	10,070
			175—185	1458	14,100
115—125	1860	2200			
125—135	1882	3666			

The movement of the mixture away from the point of ignition is checked by the restriction at 110 cm., the more so the narrower the passage, and the speed of the flame is therefore slow. When the flame has passed the restriction, however, there is no resistance

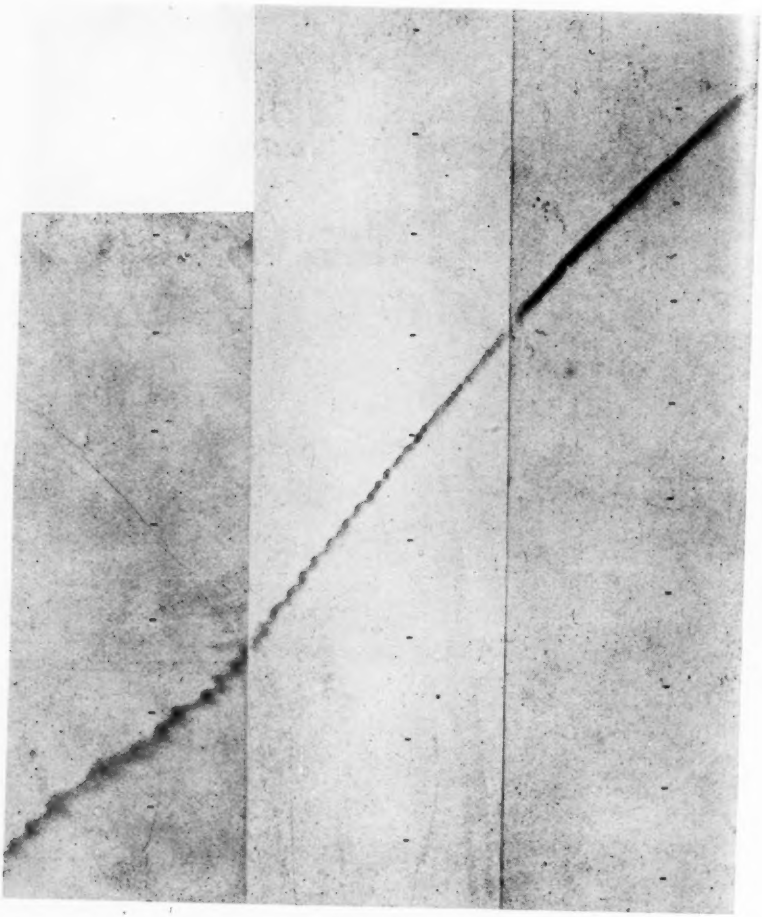
PLATE I.



1. *Tube open at both ends. Diameter reduced to* 1·5 *cm. at ignition end.*
2. *Tube open at both ends. Diameter reduced to* 2·5 *cm. at far end.*
3. *Tube closed at one end. Ignition at open end. Restrictions* 90 *and* 130 *cm. from open end.*

[*To face p.* 40.]

PLATE II.



The "uniform movement" in a 30·9% hydrogen–air mixture.

(other than frictional) to the passage of the mixture along the tube, whilst release of pressure towards the ignition end of the tube is impeded, in proportion as the aperture of the restricting ring is smaller. The speed of movement of the mixture, and thus of the flame which travels in it, therefore rapidly increases.

TABLE III.

(In sections A, B, C, and D the mean speed of flame is that measured over a distance of 30 cm. immediately beyond the last restriction.)

(A) *Diameter at ignition end reduced. Two restrictions, apertures each* 1 *cm. in diameter,* 90 *and* 130 *cm. respectively from ignition end.*

Diam. at ignition end (cm.).	2·5	1·5	1·0
Mean speed of flame (m./sec.).	131·3	58·7	Flame extinguished.

(B) *Diameter at ignition end reduced to* 2·5 *cm. One restriction* 110 *cm. from ignition end.*

Diam. of aperture of restriction (cm.).	2·5	2·0	1·5	1·0	0·5
Mean speed of flame (m./sec.).	17·3	27·0	28·7	30·1	46·0

(C) *Diameter at ignition end reduced to* 2·5 *cm. Two restrictions, apertures each* 1 *cm. in diameter, at different distances from ignition end.*

Positions of restrictions, measured from ignition end (cm.).	(i)	20	40	60	40	60	50	60	60	90	120	150
	(ii)	80	80	80	110	110	90	90	110	130	150	180
Mean speed of flame (m./sec.).		48·2	83·3	66·7	89·5	67·8	92·9	164·5	86·5	131·5	84·6	53·4

(D) *Diameter at ignition end reduced to* 2·5 *cm. Three restrictions, with apertures of different diameters, at different distances from ignition end.*

Diam. of aperture of restriction (cm.).	(i)	2·0	2·0	2·0	2·0	2·0
	(ii)	1·5	1·5	1·5	1·5	1·0
	(iii)	0·5	1·0	1·0	1·0	1·5
Positions of restrictions, measured from ignition end (cm.).	(i)	60	60	40	20	20
	(ii)	90	90	70	50	50
	(iii)	130	130	110	90	90
Mean speed of flame (m./sec.).		Flame extinguished.	60·9	100·9	75·0	83·8

(E) *Diameter at ignition end reduced to* 2·5 *cm. Two restrictions, with apertures of different diameters,* 90 *and* 130 *cm., respectively, from ignition end.* (*Mean speeds of flame between the restrictions, in cm./sec.*)

Distance from point of ignition (cm.).	95—105	105—115	115—125
Apertures 1·0 cm. diam.	1247	796	388
Apertures 1·5 cm. diam.	1182	732	461
Apertures 2·0 cm. diam.	866	709	600

When two restricting rings were present, each with apertures of 1 cm. and placed 40 cm. apart, the highest speed of flame, measured over a distance of 30 cm. just beyond the second restriction, was obtained when the ignition end of the tube was reduced in diameter to 2·5 cm., the mean value being 130 m./sec. as compared with 58·7 m./sec. when the diameter at the ignition end was 1·5 cm. Increasing the number of restrictions to three or more, the ignition end being 2·5 cm. in diameter, did not always result in an enhanced speed of flame. If the diameter of the apertures was only 1 cm., a greater number of restrictions than two decreased the speed attainable by the flame, or sometimes caused its extinction. When their aperture was 2·5 cm., three and four restrictions enabled speeds of flame of 310 and 390 m./sec., respectively, to be attained, the removal of the restriction at the ignition end reducing these velocities to 225 and 280 m./sec., respectively.

The results of typical experiments with a number of different arrangements of the restricting rings, made in an endeavour to develop the fastest flames, are given in Table III.

Beyond the first of two restrictions, the flame moves more rapidly the greater the reduction in diameter of the tube, for the reason given when considering the effect of one restriction, but the second restriction impedes the movement of the current of mixture ahead of the flame, and hence the speed is not so great as in its absence (compare Table II). The resistance offered by the second restriction is greater the smaller the aperture, so that the speed of the current, and of the flame, as it approaches the second restriction is lowest when the aperture is smallest.

(c) *The Influence of a Restriction at the Far End of the Tube.*—The result of reducing to 2·5 cm. the diameter of the end of the tube towards which the flame travelled, the ignition end remaining fully open, is recorded in Table IV.

TABLE IV.

The Effect of Restricting the Far End of a Tube Open at Both Ends.

Distance from point of ignition (cm.).	Mean speed of flame (cm./sec.). Tube fully open at both ends.	Mean speed of flame (cm./sec.). Diam. at far end reduced to 2·5 cm.	Distance from point of ignition (cm.).	Mean speed of flame (cm./sec.). Tube fully open at both ends.	Mean speed of flame (cm./sec.). Diam. at far end reduced to 2·5 cm.
5—15	106	98	85— 95	249	—
15—25	134	110	95—125	229	63
25—35	152	117	125—135	285	—
35—65	194	122	135—145	350	90
65—75	240	125	145—175	441	91
75—85	254	127	175—205	575	93

A composite photograph recording the progress of the flame throughout the length of the tube is shown in Fig. 2, Plate I. The speed of travel of the film in this photograph can be regarded as 3·5 cm./sec.

The comparatively slow speed of the flame throughout the tube can be attributed to the resistance offered by the restriction to the movement of the current of unburnt mixture ahead of the flame, the conditions approximating to those obtaining with a longer tube. In this connexion, the experiments of Mason and Wheeler (J., 1920, **117**, 36) with a tube 30·5 cm. in diameter may be recalled. When this tube, fully open at both ends, was 15·25 m. long, the flame in a 9·5% methane–air mixture travelled from end to end with increasing speed; but when the length was increased to 90 m., the general behaviour of the flame was as though the far end of the tube were closed, its velocity over the first 12—15 m. being slow and nearly uniform.

(B) *Ignition at the Open End of a Horizontal Tube Closed at the Other End.*

In an unrestricted tube, closed at one end, ignition of an inflammable mixture at the open end leads to the "uniform movement" of flame, which persists over about one-third of the length of the tube. When a restriction is introduced at some point along the tube, the movement of the flame is disturbed locally, its rate being reduced before the restriction is reached and increased over a short distance beyond it. Thus the speed of the uniform movement in a 10% methane–air mixture in the unrestricted tube was about 90 cm./sec., whereas when two restrictions were introduced reducing the diameter to 3·2 and 2·5 cm., respectively, at points 90 and 130 cm. from the open end, the velocity fell to 80 cm./sec. An acceleration occurred beyond each restriction. These effects are illustrated by Fig. 3, Plate I.* There can be no extensive movement of the mixture from an open to a closed end of a tube. The speed of the flame is therefore comparatively slow and is not greatly affected by the introduction of an impediment to movement of the mixture. The propagation of flame during the "uniform movement" is discussed later.

(C) *Ignition at the Closed End of a Horizontal Tube Open at the Other End.*

In short, wide, unrestricted tubes the fastest flame in any mixture of methane and air is normally obtained when the mixture is

* The speed of travel of the film in this photograph can be regarded as 3·0 cm./sec.

ignited at the closed end of a tube which is open at the other end. For long tubes, however, the flame becomes vibratory and does not reach the open end, because cooling of the products of combustion periodically causes a backward movement of the unburnt mixture and of the flame, with the eventual extinction of the latter by the burnt gases.

In the comparatively short tube used in these experiments, the flame was extinguished by a restriction unless this was placed fairly close to the point of ignition and its aperture was of not less than 2·5 cm. diameter. Even if these conditions were fulfilled, the introduction of a second restriction resulted in the extinction of the flame at the latter; when both apertures were 2·5 cm. in diameter and they were 80 and 120 cm. from the closed end, the mean speed of the flame increased from 26·2 to 77·5 m./sec. on passing the first restriction, whilst a retrograde secondary flame was set up at this point, as in the case of the tube open at both ends.

(D) *The "Uniform Movement" of Flame.*

We have pointed out that when a flame is travelling from an open towards a closed end of a tube there cannot, at the outset, be any extensive movement of the unburnt mixture ahead of the flame, and that the comparatively slow speed of the flame is thus explicable. Nevertheless, some movement must take place (although we have been unable to detect any current with certainty by direct measurement during the propagation of flame) and, if the assumption be correct that the speed of propagation of flame is affected under all conditions by the movement of the medium in which it travels, it is not to be expected that there should be a strictly "uniform movement" of flame over one-third the length of the tube. Rather would one expect an initial acceleration, slight but appreciable, followed by an equally slight retardation.

With a view to detect slight departures from strict uniformity of movement, we photographed the flame travelling in a 9·75% methane–air mixture over the first 80 cm. of the tube, on a film revolving at such a rate that slight differences in the velocity of the flame could readily be measured. The results are recorded in Table V.

TABLE V.

The Uniform Movement of Flame in a 9·75% Methane–Air Mixture.

Distance along tube (cm.).	0—10	10—20	20—30	30—40	40—50	50—60	60—70	70—80
Speed of flame (cm./sec.).	87·7	89·45	91·5	92·5	91·75	91·2	90·8	90·55

Although the speed of the flame is nearly uniform, there are just such slight variations as would be anticipated if some motion, affecting the speed of the flame, were imparted to the mixture. In conformity with the general argument now advanced, the implication is that the speed of the uniform movement of flame is compounded of (1) the normal rate of propagation of flame by conduction of heat, and (2) the initial motion of the unburnt mixture towards the closed end of the tube. The speed of the latter should increase with increase in the diameter of the tube. There should therefore be a definite relationship between the speed of " uniform movement " of flame in a given mixture and the diameter of the tube in which it travels.

Such determinations for mixtures of 10% of methane in air were made by Mason and Wheeler (J., 1917, **111**, 1044) for the last five tubes shown in Table VI and by Payman and Wheeler (J., 1918, **113**, 656) for the smaller tubes.

TABLE VI.

The Uniform Movement of Flame in Tubes of Different Diameters.
10% *Methane–Air Mixture.*

Diam. of tube (cm.).	0·45	0·56	0·72	0·81	0·90	2·5	5·0	9·0	30·5	96·5
Speed of uniform movement (cm./sec.).	33·5	41·2	46·3	47·4	48·0	66	92	104	168	250

On plotting the logarithm of the diameter of the tube against that of the flame-speed, the points are found to lie on a straight line. There appears, therefore (for the range of diameters considered), to be a relationship between the speed of the uniform movement of flame, V, and the diameter, D, of the tube in which it travels, of the form $V = cD^k$, k and c being constants.

Mason and Wheeler, in their discussion of the cause of variation of the speed of the uniform movement with the diameter of the tube (*loc. cit.*, p. 1052), assumed that when the diameter exceeds 10 cm. the speed is affected by the coming into play of heat transference by convection. It is clear from the relationship now given, whatever may be its full meaning, that such an assumption is unnecessary, and that no new factor affecting the propagation of flame is introduced after a certain diameter of tube is exceeded. Further, if it be correct to regard this relationship as indicating the effect of increased diameter on the speed of movement of the medium in which the flame travels, a satisfactory explanation, hitherto lacking, is available for the increased speed observed with increased diameter of tube when the flame is propagated downwards from an open towards a closed end (J., 1920, **117**, 1227)—

conditions which should render the effects of heat transference by convection negligible.

Although this communication is directly concerned only with the propagation of flame in mixtures of methane and air, it is not out of place to refer to recent experiments in which Miss E. H. M. Georgeson and Mr. F. J. Hartwell, by photographic analysis, determined the speed of the "uniform movement" in mixtures of hydrogen and air, for they have a direct bearing on the suggestion that the mixture in which the flame is moving is itself in motion. The results are of particular interest to us since they exhibit the initial acceleration of speed, followed by a retardation, which we anticipated; presumably because of the lesser density of the medium in which the flame is travelling, these phenomena are more marked than with mixtures of methane and air (see Table V). We are indebted to Miss Georgeson and Mr. Hartwell for the composite photograph reproduced as Plate II (about $\frac{1}{3}$ its original size), which illustrates admirably the changes of speed during the "uniform movement" of flame in a 30·9% hydrogen–air mixture. The mixture was contained in a horizontal tube of fused silica, 2·5 cm. in diameter, and the flame was photographed through a quartz lens on Lumière paper attached to a drum revolving at such a high speed as to render accurate analysis of the rapid movement possible. The flame is shown travelling from right to left over the first 78 cm. The time-intervals recorded are 0·02 of a second.

We are indebted also to Professor Statham, of this University, who has made a particular study of the problems of mine ventilation, for experimental evidence that in a tube open at one end and closed at the other an appreciable movement of a column of air takes place towards the closed end if a small pressure difference is created at the open end.

These experiments form part of a research that we are carrying out for the Safety in Mines Research Board, to whom our thanks are due for permitting publication.

Department of Fuel Technology,
Sheffield University. [*Received, September 27th*, 1926.]

VII.—*The Oxidation of Nitrophenylcyanoacetates.*

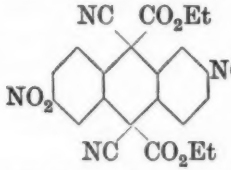
By Arthur Fairbourne and Harold Richard Fawson.

During an investigation on possible methods of synthesising substituted anthracenes (J., 1921, **119**, 1573; 1923, **123**, 1137), certain nitrophenylcyanoacetates were prepared and their hydrolytic

and oxidation products examined. Ethyl sodiocyanoacetate was condensed with picryl chloride, 2 : 4-dinitrochlorobenzene and *p*-nitrochlorobenzene, producing ethyl 2 : 4 : 6-trinitrophenylcyanoacetate, ethyl 2 : 4-dinitrophenylcyanoacetate and ethyl *p*-nitrophenylcyanoacetate, respectively.

On oxidation, these nitrophenyl derivatives of ethyl cyanoacetate should produce first the hydroxy-esters, $R{\cdot}C(OH)(CN){\cdot}CO_2Et$ (Meyer, *Ber.*, 1878, **11**, 1283; 1879, **12**, 2238), which would then be capable (i) of losing hydrogen cyanide and becoming ketonic esters, $R{\cdot}CO{\cdot}CO_2Et$, (ii) of reacting with unoxidised material to yield substituted succinic esters (I), or (iii) of condensing to form substituted anthracenes (II) of a particularly interesting type (compare Barnett, " Anthracene and Anthraquinone," pp. 50, 69).

(I.) $\begin{matrix} R{\cdot}C(CN){\cdot}CO_2Et \\ | \\ R{\cdot}C(CN){\cdot}CO_2Et \end{matrix}$



(II.)

Of these possibilities, (i) and (ii) have been realised. Under identical conditions, ethyl *p*-nitrophenylcyanoacetate was oxidised by chromic anhydride to the substituted succinic ester (I; $R = C_6H_4{\cdot}NO_2$), which was independently synthesised and its constitution verified; ethyl 2 : 4-dinitrophenylcyanoacetate gave the ketonic ester, $C_6H_3(NO_2)_2{\cdot}CO{\cdot}CO_2Et$; and ethyl 2 : 4-dinitrobromophenylcyanoacetate yielded the intermediate hydroxy-ester, $C_6H_2Br(NO_2)_2{\cdot}C(CN)(OH){\cdot}CO_2Et$.

These nitrophenylcyanoacetates are all colourless or slightly yellow in the solid state and in dry organic solvents, but some of them develop intense colour in the presence of water and all do so when treated with alkalis.

Experimental.

Ethyl 2 : 4-*Dinitrophenylcyanoacetate*, $C_6H_3(NO_2)_2{\cdot}CH(CN){\cdot}CO_2Et$. —To a solution of 2·3 g. of sodium in 40 c.c. of alcohol, 11·3 g. of ethyl cyanoacetate were added, followed by a solution of 10 g. of 2 : 4-dinitrochlorobenzene in 30 c.c. of alcohol. After the resulting red mixture had been refluxed on a water-bath for 4—5 hours, the alcohol was removed, 600 c.c. of water added, and the whole acidified with dilute nitric acid. The brown oil that separated was isolated by means of ether and, after solidifying, crystallised several times from alcohol–ligroin. The *ester* was thus obtained in colourless, crystalline needles, m. p. 66° (yield, 90%) (Found: C, 47·1; H, 3·6; N, 15·1. $C_{11}H_9O_6N_3$ requires C, 47·3; H, 3·2; N, 15·1%).

Its structure was proved by hydrolysis with concentrated hydrochloric acid; the 2 : 4-dinitrophenylacetic acid obtained melted at 179° (decomp.), alone or mixed with an authentic specimen (Radziszewski, *Ber.*, 1869, 2, 210).

The ester gave a red solution in wet alcohol and a purple solution in concentrated sulphuric acid. Its *sodium* derivative was precipitated as a red explosive powder when the ester was treated with the theoretical weight of sodium dissolved in alcohol, and ether added (Found : Na, 7·3. $C_{11}H_8O_6N_3Na$ requires Na, 7·6%). The sodium could not be replaced directly by a radical, but was replaced by silver and then by the ethyl group.

Ethyl 2 : 4-*Dinitrophenylethylcyanoacetate*.—From the preceding sodium derivative and silver nitrate in aqueous solution, the corresponding *silver* derivative was obtained as a red powder. This was dried, and treated with an excess of ethyl iodide; after some time, ether was added and the solution was filtered and evaporated. The residual red oil, which solidified, crystallised from alcohol in colourless plates, m. p. 98° (Found : C, 50·6; H, 4·7. $C_{13}H_{13}O_6N_3$ requires C, 50·8; H, 4·2%).

2 : 4-*Dinitrophenylacetonitrile* was obtained when ethyl 2 : 4-dinitrophenylcyanoacetate was boiled with dilute hydrochloric acid during 2—3 hours. It was isolated as an oil by means of ether and crystallised from carbon tetrachloride in yellow needles, m. p. 89° (Found : C, 46·1; H, 2·6; N, 20·2. $C_8H_5O_4N_3$ requires C, 46·4; H, 2·4; N, 20·3%). Its solution in hot water was colourless but became green on the addition of alkali.

Ethyl p-*nitrophenylcyanoacetate* was prepared in the same way as the dinitro-compound, a solution of 8 g. of *p*-nitrochlorobenzene in 20 c.c. of alcohol being used and what was unchanged being filtered off before the addition of nitric acid. The product, a brown oil which could not be solidified, was converted into its *sodium* derivative in the way described above (Found : Na, 9·0. $C_{11}H_9O_4N_2Na$ requires Na, 9·0%).

The crude ester was hydrolysed with dilute and with concentrated hydrochloric acid, which produced, respectively, *p*-nitrophenylacetonitrile, m. p. 114° (compare Radziszewski, *Ber.*, 1870, 3, 198), and *p*-nitrophenylacetic acid, m. p. 152° (Radziszewski, *Ber.*, 1869, 2, 209). The latter was further identified by a mixed melting-point determination with an authentic specimen.

Ethyl 2 : 4 : 6-*trinitrophenylcyanoacetate* also was prepared by the same method, a solution of 12·4 g. of picryl chloride in 60 c.c. of alcohol being used. The colourless product (8·7 g.) crystallised from alcohol-ligroin in faintly pink needles, m. p. 95°, which formed red and purple solutions in water and concentrated sulphuric acid,

respectively (Found: C, 40·9; H, 3·2; N, 17·5. $C_{11}H_8O_8N_4$ requires C, 40·7; H, 2·5; N, 17·3%).

Ethyl αβ-*Di*-p-*nitrophenyl*-αβ-*dicyanosuccinate* (I; R = $C_6H_4{\cdot}NO_2$). —Ethyl *p*-nitrophenylcyanoacetate (1·5 g.) or its sodium derivative was refluxed with a solution of 2·5 g. of chromic anhydride in 20 c.c. of glacial acetic acid for ¾ hour. The white solid obtained by pouring the product into cold water crystallised from glacial acetic acid in colourless needles, m. p. 209° (Found: C, 57·2; H, 3·5; N, 12·1; *M*, cryoscopic in benzene, 451. $C_{22}H_{18}O_8N_4$ requires C, 56·7; H, 3·9; N, 12·1; *M*, 466), which gave a series of colour changes when warmed with alcoholic potash.

The ester was unattacked by hot concentrated hydrochloric or nitric acid, and was easily precipitated from the latter in a very pure state. Its structure was proved as follows: 4·5 g. of the silver derivative of ethyl *p*-nitrophenylcyanoacetate, prepared from the sodium derivative by the action of silver nitrate, were heated under reflux for ½ hour with a solution of 1·7 g. of iodine in ether. The silver iodide produced and the ether were removed and the residue, after being washed with alcohol to remove the excess of iodine, was crystallised twice from alcohol and once from glacial acetic acid; the needles thus obtained melted at 209°, alone or mixed with the specimen described above.

Ethyl 2 : 4-*dinitrobenzoylformate*, $C_6H_3(NO_2)_2{\cdot}CO{\cdot}CO_2Et$, was obtained by boiling a solution of 1·5 g. of ethyl 2 : 4-dinitrophenylcyanoacetate and 2·3 g. of chromic anhydride in glacial acetic acid for 1 hour. The colourless solid obtained by pouring the product into water was crystallised from alcohol; m. p. 89° (Found: C, 44·7; H, 3·35; N, 10·85; *M*, cryoscopic in benzene, 245. $C_{10}H_8O_7N_2$ requires C, 44·8; H, 3·0; N, 10·45%; *M*, 268). The *phenylhydrazone* separated from the mixture when 1 g. of the ester was heated on a water-bath for ¼ hour together with 10 drops of phenylhydrazine dissolved in dilute acetic acid; it crystallised from alcohol in golden needles, m. p. 170° (Found: N, 15·1. $C_{16}H_{14}O_6N_4$ requires N, 15·6%). A small amount of red substance, obtained on diluting the filtrate, melted, after recrystallisation from alcohol, at 139°. By fusing it with the product of m. p. 170° it was converted into the latter, indicating that it was probably another form of the phenylhydrazone.

Ethyl 2 : 4-*dinitrobromophenylcyanoacetate* was prepared by boiling the sodium derivative of ethyl 2 : 4-dinitrophenylcyanoacetate with excess of bromine dissolved in moist ether. It crystallised from alcohol in needles, m. p. 98° (Found: C, 36·9; H, 2·7; N, 12·3; Br, 21·9. $C_{11}H_8O_6N_3Br$ requires C, 36·9; H, 2·2; N, 11·7; Br, 22·3%). This compound was originally prepared by accident in an

attempt to oxidise ethyl 2 : 4-dinitrophenylcyanoacetate by bromine instead of by chromic anhydride. That the bromine atom is in the ring was established by the preparation of the following oxidation product.

Ethyl 2 : 4-*dinitrobromophenylhydroxycyanoacetate*,

$$C_6H_2Br(NO_2)_2 \cdot C(OH)(CN) \cdot CO_2Et,$$

was produced when ethyl 2 : 4-dinitrobromophenylcyanoacetate was treated with chromic anhydride under the conditions described for the previous oxidations. It crystallised from alcohol in colourless needles, m. p. 157° (Found : C, 35·3; H, 2·9; N, 12·6; Br, 21·4. $C_{11}H_8O_7N_3Br$ requires C, 35·3; H, 2·1; N, 11·2; Br, 21·4%).

Ethyl 2 : 4-*dinitrochlorophenylcyanoacetate* was prepared by passing chlorine into an aqueous solution of the sodium derivative of ethyl 2 : 4-dinitrophenylcyanoacetate until the red colour had been destroyed. It crystallised from alcohol in needles, m. p. 101° (Found : Cl, 11·3. $C_{11}H_8O_6N_3Cl$ requires Cl, 11·3%). The structure of this compound would appear to be sufficiently established by analogy with the corresponding bromo-derivative mentioned above. Its action with chromic anhydride is under investigation.

The authors wish to express their indebtedness to the Chemical Society for a grant to one of them (A. F.) which partly defrayed the expenses incurred in this work.

KING'S COLLEGE, LONDON, W.C. 2. [*Received, October 16th*, 1926.]

VIII.—*Studies in Optical Superposition. Part VIII. The* l-*Menthylamine, Brucine, and Strychnine Salts of Mucic and* allo*Mucic Acid.*

By THOMAS STEWART PATTERSON and JAMES DAVIDSON FULTON.

IN Part VII (J., 1926, 3224) and previous papers attempts were made to attack the problem of optical superposition by what seemed the simplest method capable of yielding positive results, namely, the preparation of esters formed from the *d*-, the *l*-, and the *i*-modifications of tartaric acid or some of its derivatives, with an active alcohol such as *l*-menthol or one of the methyl-*n*-hexylcarbinols. If the principle of optical superposition really holds, the mean of the rotations of such *d*- and *l*-compounds should be identical with that of the *i*-compound. This method sometimes presents considerable practical difficulties, and of course involves in the end result a possible summation of the experimental errors for the three different esters.

A method of obtaining further data on this problem would be

the comparison of the rotations of esters of mucic and *allo*mucic acid, respectively, with active alcohols. These two acids are both optically inactive, their inactivity being due to compensation, in two different ways, of the activities due to the asymmetric carbon atoms. If the rotation of, say, *l*-menthyl mucate is different from that of *l*-menthyl *allo*mucate, this difference can hardly be ascribed to anything else than the different arrangement of the groups attached to the asymmetric carbon atoms in the mucic and *allo*-mucic acids; and such a difference, we consider, would be a sound disproof of van 't Hoff's conception. Unfortunately, our attempts to prepare menthyl mucate and menthyl *allo*mucate by heating together the respective acids and the alcohol, under the influence of dry hydrogen chloride, have failed, but we have prepared some salts of these acids with active bases as described below. The salts of active acids are not so suitable for our purpose as the esters would have been; the results arrived at from rotation values obtained in aqueous solution, on the one hand, might easily be complicated by the influence of electrolytic dissociation, whilst, on the other, the solubility of such salts as we have been able to prepare is usually only slight in non-dissociating solvents. Nevertheless, we have determined the rotations of the brucine, the strychnine, and the *l*-menthylamine salts of mucic acid and of *allo*mucic acid, either in methyl alcohol or in benzyl alcohol. We prepared also the corresponding salts of nicotine, codeine, and morphine, but these were difficult to purify in a satisfactory manner and were not further examined. As a check on our results, the preparation of each salt and its optical examination were carried out twice; these preparations are indicated below as *A* and *B*.

allo*Mucic acid* was prepared according to Emil Fischer (*Ber.*, 1891, **24**, 2136) by heating mucic acid in aqueous pyridine solution in a copper autoclave. M. p. 172—173°.

Menthylamine Mucate.—To the acid (1 mol.) in hot water was added menthylamine (2 mols.), $\alpha^{19°}_{5461}$ (homogeneous: $l = 100$ mm.) −35·31°, *d* 0·8574, $[\alpha]^{19°}_{5461}$ −41·2°. This furnished a salt which, after two crystallisations from water, formed plates, m. p. 198° (decomp.) [Found: N, (*A*) 5·4, 5·4, (*B*) 5·4. $C_6H_{10}O_8,2C_{10}H_{21}N$ requires N, 5·4%]. $\alpha^{19·5°}_{5461}$ (methyl alcohol: $c = 1$; $l = 400$ mm.) = −1·29° for *A* and −1·27° for *B*.

Menthylamine allo*mucate* was prepared in the same way as the mucate. Fine needles, m. p. 173° (decomp.) [Found: N, (*A*) 5·5, 5·4, (*B*) 5·4%]. $\alpha^{19·5°}_{5461}$ (methyl alcohol: $c = 1$; $l = 400$ mm.) = −1·26° for *A* and −1·24° for *B*.

The brucine salts were prepared similarly from purified brucine of m. p. 177—178° and $\alpha^{17·3}_{5461}$ (ethyl alcohol: $c = 3·008$; $l = 100$ mm).

$= -2{\cdot}97°$, whence $[\alpha]_{5461}^{17{\cdot}3°} = -98{\cdot}74°$; after recovery from the salts, its m. p. was 176° and $\alpha_{5461}^{18°}$ (ethyl alcohol : $c = 3{\cdot}008$; $l = 100$ mm. $= -2{\cdot}94°$, whence $[\alpha]_{5461}^{18°} = -97{\cdot}75°$.

Brucine mucate, crystallised twice from water, formed needles which commenced to froth about 150° [Found in specimens dried for a long time in a vacuum over sulphuric acid : N, (*A*) 5·6, 5·8, (*B*) 5·7. $2C_{23}H_{26}O_4,C_6H_{10}O_8$ requires N, 5·6%]. In benzyl alcohol ($c = 5$; $l = 400$ mm.), $\alpha_{5461}^{17°}$ for $A = +0{\cdot}27°$ and $\alpha_{5461}^{20°}$ for $B = +0{\cdot}23°$, whence $[\alpha]_{5461}^{17°}$ and $[\alpha]_{5461}^{20°} = +1{\cdot}35°$ and $+1{\cdot}15°$, respectively. After some time, a fine precipitate settled on the walls of the tube and the rotation altered.

Brucine allo*mucate* formed needles which, after two crystallisations from water, decomposed at 170°, softening at a lower temperature [Found : N, (*A*) 5·7, 5·8, (*B*) 5·7%]. In benzyl alcohol ($c = 5$; $l = 400$ mm.), $\alpha_{5461}^{17°}$ for $A = -0{\cdot}22°$ and $\alpha_{5461}^{20°}$ for $B = -0{\cdot}19°$, whence $[\alpha]_{5461}^{17°}$ and $[\alpha]_{5461}^{20°} = -1{\cdot}10°$ and $-0{\cdot}95°$, respectively.

The *strychnine* salts were prepared from purified strychnine of m. p. 284° and $\alpha_{5461}^{20°}$ (chloroform : $l = 100$ mm.; $c = 5{\cdot}02$) $= -8{\cdot}61°$, whence $[\alpha]_{5461}^{20°} = -171{\cdot}5°$; after recovery from the salts, its m. p. was unchanged and $[\alpha]_{5461}^{19{\cdot}5°} = -169{\cdot}7°$.

Strychnine mucate, twice recrystallised from water, formed fine needles which became brown at 200° and decomposed at 273°. The compound had previously been prepared by Ruhemann and Dufton (J., 1891, 59, 750) [Found : N, (*A*) 6·35, 6·4, (*B*) 6·4. Calc. for $2C_{21}H_{22}O_2N_2,C_6H_{10}O_8$: N, 6·4%]. $\alpha_{5461}^{17{\cdot}5°}$ (benzyl alcohol : $l = 400$ mm.; $c = 3{\cdot}5$) for $A = +1{\cdot}11°$, whence $[\alpha]_{5461}^{17{\cdot}5°} = +7{\cdot}93°$, and $\alpha_{5461}^{21{\cdot}5°}$ (benzyl alcohol : $l = 400$ mm.; $c = 5$) for $B = +1{\cdot}06°$, whence $[\alpha]_{5461}^{21{\cdot}5°} = +7{\cdot}57°$.

Strychnine allo*mucate*, twice crystallised from water, formed needles turning brown at 189°, and decomposing at 269° [Found : N, (*A*) 6·4, 6·45, (*B*) 6·4%]. In benzyl alcohol ($c = 3{\cdot}5$; $l = 400$ mm.), $\alpha_{5461}^{17{\cdot}5°}$ for $A = +0{\cdot}99°$ and $\alpha_{5461}^{21{\cdot}5°}$ for $B = +0{\cdot}96°$, whence $[\alpha]_{5461}^{17{\cdot}5°}$ and $[\alpha]_{5461}^{21{\cdot}5°} = +7{\cdot}07°$ and $+6{\cdot}86°$, respectively.

The results of these experiments are tabulated :

Specific Rotation for Mercury Green Light. Temperature about 20°.

	Menthylamine.	Δ.	Brucine.	Δ.	Strychnine.	Δ.
First series.						
Mucic acid	−32·25°	0·75°	+1·35°	2·45°	+7·93°	0·86°
*allo*Mucic acid	−31·50		−1·10		+7·07	
Second series.						
Mucic acid	−31·75	0·75	+1·15	2·11	+7·57	0·71
*allo*Mucic acid	−31·00		−0·96		+6·86	

Regarding these results, it may be noted particularly that the rotations of the brucine and strychnine salts of mucic and *allo*mucic acid are remarkably low in view of the highly active character of the bases and the inactivity of the acids. This might well suggest the idea that in combination with certain active bases the asymmetric carbon atoms of the acid molecule no longer neutralise each other in pairs, but that the acid part of the molecule has become active and is contributing to the rotation. This, if it be the case, is, of course, in strong opposition to the principle of optical superposition. A similar observation was made in Part V of this series (J., 1924, **125**, 578), where the specific rotation, $[\alpha]^{17°}_{5461}$, of *d-sec.*-octyl *i*-tartrate was found to be only 0·18°. The menthylamine salts show a similar tendency, but not so markedly.

It will be seen from the third column of the table that the difference found between the specific rotations of the menthylamine salts of mucic and *allo*mucic acid is only small, 0·75°, but it is the same in both series, and greater, although not much, than the difference which was found between the rotations for like salts of one of the acids in the two series of experiments. It is, therefore, presumably greater than the experimental error.

The difference for the brucine salts is also nearly the same in the two series of experiments, but it is specially remarkable that the two salts are active in opposite senses. This seems to be a really strong argument against the principle of optical superposition. With reference to the strychnine salts, it may be noted, firstly, that the rotations are both positive, and secondly, that although the absolute difference is not very great, it is at least twice the probable experimental error and fairly large in proportion to the actual rotations of the individual compounds.

Thus, although the results for the menthylamine and strychnine salts are hardly as definite as might be desired, they certainly do not seem to support the idea that the configuration of mucic acid has exactly the same effect as that of *allo*mucic acid in determining the rotation of compounds formed from these acids and one and the same active base, whilst the results with the brucine salts are definitely in conflict with van 't Hoff's supposition.

UNIVERSITY OF GLASGOW. [*Received, November 30th*, 1926.]

IX.—*Optical Activity and the Polarity of Substituent Groups. Part VI. Optically Active Acids and Bases.*

By Harold Gordon Rule.

In the first paper of this series (J., 1924, **125**, 1121), it was shown, from a consideration of the relative directive effects of a number of substituents on benzene substitution, that the substituents could be arranged in a *polar series* representing a gradual transition from those of high positive polarity through the comparatively non-polar groups to those of high negative polarity. This series was also found to correspond with the influence of the same substituents on the rotatory powers of certain aliphatic and aromatic compounds, special reference being made to the menthyl esters of ortho-substituted benzoic acids. A theoretical justification for this series was based on the views of Sir J. J. Thomson on the nature of substitution in organic compounds (*Phil. Mag.*, 1923, **46**, 497).

In the main, these conclusions have been supported by further experiments with the menthyl and *sec.*-β-octyl esters of *o*-substituted benzoic acids (Rule and Smith, J., 1926, **553**; Rule and Numbers, *ibid.*, 2116), although where the substituents are separated from the asymmetric atom by a longer non-conjugated chain their influence on the rotatory power is more closely related to their *general effect* as deduced from data referring to the dissociation constants of acids. Under the latter heading may be mentioned the derivatives of active bases investigated by Betti (*Gazzetta*, 1923, **53**, 417) and the menthyl and *sec.*-β-octyl esters of monosubstituted acetic acids (Rule and Smith, J., 1925, **127**, 2188; Rule and Mitchell, J., 1926, 3202). The deductions previously drawn from Thomson's views on *m*- and *p*-disubstituted benzenes have not been confirmed, however, and from an investigation on the inductive capacities of *o*-, *m*-, and *p*-disubstituted benzenes recently carried out in these laboratories, Kerr (*Phil. Mag.*, in the press) concludes that Thomson's suggestions only hold in their original simplicity for compounds of this type in which the two substituents are identical.

Now if the properties of compounds are affected in the manner indicated above by the polarity of substituent groups, it would be anticipated that changes of an even more pronounced character would follow the introduction into the molecule of ionisable complexes which are capable of assuming an actual electrical charge. It is an accepted fact that an ionised complex exerts a powerful influence on substitution in the benzene nucleus, and that the course of this reaction varies with the sign of the charge. For

example, although aniline under ordinary conditions substitutes in the *o*-, *p*-positions, it may be nitrated in the *m*-position by using it in the form of aniline sulphate dissolved in a large excess of sulphuric acid. The positively charged ionic complex $\cdot NH_3^+$ thus behaves as a positive or *m*-directive substituent. On the other hand, benzoic acid, which brominates slowly in the *m*-position, may be rapidly converted into the *o*- and *p*-derivatives by chlorinating the sodium salt in aqueous solution (Lossen, D.R.-P. 146174). Here the negatively charged complex $\cdot CO \cdot O^-$ ranges itself with the negative or *o*-, *p*-directive substituents. The parallel between the influence of substituents on the nitration of a mono-substituted benzene and on the optical activity of esters of *o*-substituted benzoic acids is illustrated in the following table, where (*a*) represents the percentage of *m*-compound formed, (*b*) percentage of *p*-compound, (*c*) molecular rotations of the menthyl esters, and (*d*) molecular rotations of the *sec.*-β-octyl esters, in so far as these values have been determined.

Table of Substituent Influence.

	NH_3^+.	NO_2.	CO_2H.	COMe.	H.	Me.	I.
a	{Chiefly meta}	93	76	55	—	3·1	—
b	{Chiefly meta}	0·4	1·2	—	—	41	66
c	—	381°	332°	261°	239°	231°	237°
d	—	122°	(90—117°*)	—	78°	—	—

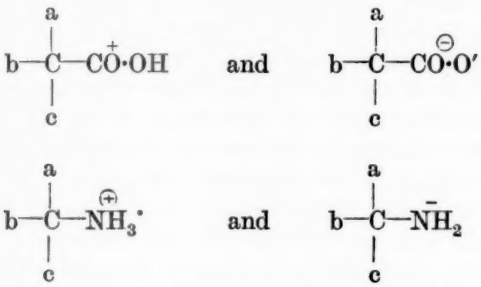
	Br.	Cl.	F.	$CO \cdot O^-$.	OMe.	NMe_2.
a	0·3	—	0·2			
b	62	70	87	(Chiefly para and ortho.)		
c	205°	195°	194°	180°	148°	101°
d	—	47°*	—	—	33°	—

* Rule, Numbers, and Paterson, unpublished results.

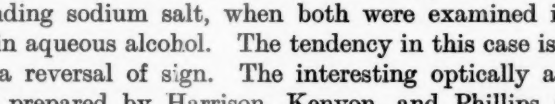
The parallel is a very complete one, and particular attention may be directed to the difference in the behaviour of the positive carboxyl group and the negatively charged $\cdot CO \cdot O^-$ complex. The value of 180° is quoted for the rotation of the sodium salt of menthyl hydrogen phthalate in 5% aqueous solution (Kenyon and Pickard, J., 1915, **107**, 58), but it is probable that this falls to a still lower limiting value at greater dilutions. No figures are yet available for the rotation of menthyl *o*-dimethylaminobenzoate in acid solution. It may, however, be predicted that this will be higher than that for the free basic ester, and probably higher than the value for the unsubstituted menthyl benzoate, if the hydrochloride is sufficiently ionised under the conditions of experiment.

The influence of an ionisable group should also be recognisable in a simple type of compound in which the remaining three groups attached to the asymmetric atom are of a comparatively non-polar character. In this connexion, it is common knowledge among

workers with optically active substances that the rotations of simple active acids and bases often diminish in magnitude and frequently undergo a reversal of sign when the compounds are converted into the ionised state. This is precisely what might be expected, particularly if the acidic or basic group is the only group of high polar character in the molecule.



Among optically active acids undergoing a reversal of this kind may be mentioned the lactic, glyceric, and methoxysuccinic acids. Phenylpropylacetic acid (Pickard and Yates, J., 1909, **95**, 1011), having a molecular rotation of $[M]_D = 140{\cdot}7°$ in benzene and $104{\cdot}7°$ in chloroform, gives a sodium salt of $[M]_D = 5{\cdot}0°$ in water. Benzylmethylacetic acid increases somewhat in rotation on being converted into its sodium salt. Numerous salts of *d*-valeric acid are described in the literature, but no mention is made of their rotatory power. A specimen of commercial valeric acid in the author's possession, however, had a specific rotation almost exactly double that of the corresponding sodium salt, when both were examined in a 10% solution in aqueous alcohol. The tendency in this case is therefore towards a reversal of sign. The interesting optically active sulphoxides prepared by Harrison, Kenyon, and Phillips (J., 1926, 2079), in which the ionisable groups are separated from the asymmetric sulphur atom by a benzene nucleus, behave in the same manner. *d*-*m*-Carboxyphenyl methyl sulphoxide has a lower rotation in the form of its sodium salt, and *l*-4′-amino-4-methyldiphenyl sulphoxide suffers a reversal of the sign of rotation in hydrochloric acid solution.



Other typical optically active bases which show a reversal of sign on being converted into their hydrochlorides are lævorotatory amylamine and *l*-nicotine. On the other hand, *d*-butyl*iso*butylacetic acid is recorded as having a specific rotation of + 6·3° in xylene, + 6·0° in alcohol, and + 7·1° in an equivalent amount of aqueous

sodium hydroxide (Fischer, Holzapfel, and Gwinner, *Ber.*, 1912, 45, 250). No figures are available for the salt and the acid in the same solvent.

In the majority of cases, the ionisation of an active carboxylic acid appears to lead to a smaller change in rotatory power than the ionisation of an active base. Probably one factor contributing towards the weaker effect of the electrolytically dissociated carboxyl group is that the atom bearing the charge is one remove further away from the asymmetric centre than that in the corresponding base.

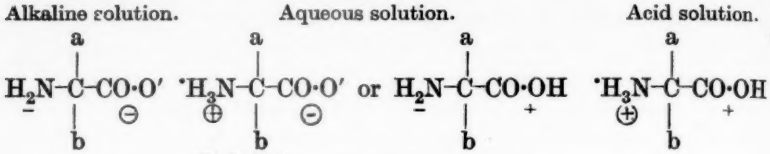
A more definite example of the change in the polar influence of the amino-group on ionisation is to be found in the rotatory powers of derivatives of active amyl alcohol, although it is doubtful if some of these have yet been obtained in a state of optical purity.

Molecular Rotations of Amyl Derivatives, $C_5H_{11}X$.

X.	$\cdot NH_3^+$.	CO_2H.	I.	Et.	Br.	Cl.	OMe.	OH.	NH_2.
[*M*]	+11·20°	+10·5°	+11·17°	+6·2°	+5·6°	+1·8°	+0·41°	−5·1°	−5·2°

An examination of the figures reveals a close analogy with those relating to the menthyl benzoates and to benzene substitution. Here again the substituents arrange themselves into the polar series, having at the one end the positively charged ionic complex $\cdot NH_3^+$ and the carboxyl group, and at the other end the negative amino- and hydroxyl groups. The value quoted for the carboxylic compound is certainly too low (compare J., 1924, 125, 1121) and possibly the rotation of the amine hydrochloride would also be increased under conditions leading to more complete ionisation. These figures illustrating the reversal in the influence of the amino-group when ionised supplement those recorded above for the carboxyl group in the menthyl benzoates.

Additional support for this explanation of the behaviour of optically active acids and bases may be found in the variations undergone by the rotatory powers of active amino-acids in alkaline, neutral and acid solution. An amino-acid in aqueous solution is in only a very slightly ionised state. On making such a solution alkaline, the result, on the whole, is to convert the positive carboxyl group more or less completely into the negatively charged complex $\cdot CO \cdot O'$. On the other hand, the addition of hydrochloric acid to the aqueous solution results in the more complete ionisation of the amino-group, transforming it from a negative substituent into one of positive polarity. These changes go hand in hand with alterations in rotatory power, as may be seen from the following figures referring to the specific rotations of aspartic acid and asparagine. In the formulæ an encircled positive or negative sign represents an ionised complex.



d-Aspartic acid.	−9·02° (1 mol. NH_3)	+4·36°	+30·0° (1 mol. HCl)
l-Asparagine.	−8·64° (1 mol. NaOH)	−5·30°	+26·4° (1 mol. HCl)

Exceptional behaviour is shown by *l*-leucine, which is recorded as being lævorotatory in aqueous solution and dextrorotatory in both acid and alkaline solutions. Taken in conjunction with the case of *d*-butyl*iso*butylacetic acid already mentioned, this suggests that there is a disturbing factor in the rotatory powers of these two acids, due to the critical length of the butyl chain.

It is evident that the presence or absence of groups of marked polarity is one of the main factors governing the rotatory power of an optically active compound, and already it seems possible to discern at least three ways in which their influence may be brought to bear on the asymmetric atom. The polar influence may be intramolecular and transmitted either through the chain of atoms or through space, as in the case of the menthyl benzoates and amyl derivatives quoted. A second effect, studied by Frankland, Pickard and Kenyon, Hilditch, and others, may lead to a sudden change in activity as the chain attached to the asymmetric centre attains a length of 5, 10, or 15 atoms. This effect is apparently due to the end of the chain coming into close proximity to the asymmetric atom and is therefore intramolecular and transmitted through space. In addition, it is probable that polar groups, whether present in the asymmetric compound or in the solvent, also exert an influence on neighbouring molecules, leading to corresponding changes in rotatory power. Some evidence on this point is provided by the fact that the substituents of the series H < Me < OMe < Cl < Br < I exert a graded influence in the sense indicated on the molecular rotations of the *sec.*-β-octyl acetates, $CH_2X{\cdot}CO{\cdot}O{\cdot}C_8H_{17}$, and that the influence of the solvents C_6H_5X on each of these esters is given by practically the same sequence, *viz.*, Me < H < OEt < Cl < Br < I (Rule and Mitchell, J., 1926, 3202).

Summary.

1. It has previously been shown that substituents may be arranged into a polar series representing a gradual transition from high positive, through neutral, to high negative polarity, and that this series corresponds to the relative influence of the substituents on

benzene substitution and the rotatory power of a number of optically active compounds.

2. It is now pointed out that the positively charged ionic complex $-NH_3^{\cdot}$ ranges itself with the positive substituents and the negatively charged complex $-CO{\cdot}O'$ with the negative substituents in their influence on rotatory power and benzene substitution.

3. This extension of the original theory is shown to explain the behaviour of a number of optically active bases, acids, and amino-acids on ionisation.

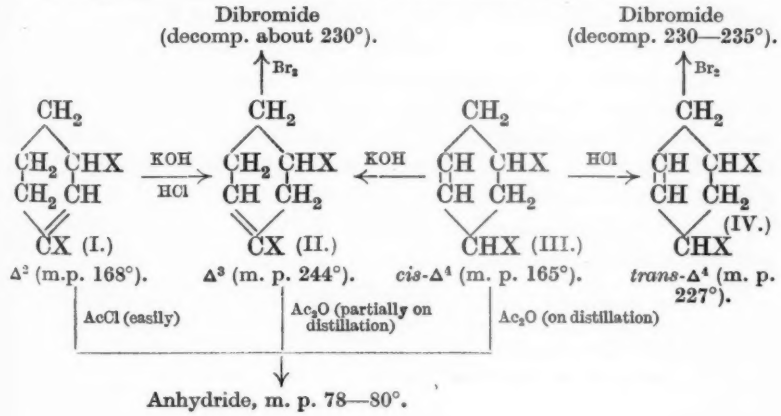
4. Three ways are suggested by which the polar effect may be transmitted to the asymmetric atom.

UNIVERSITY OF EDINBURGH. [*Received, November 27th*, 1926.]

X.—*The Chemistry of the Glutaconic Acids. Part XXI. Non-formation of* Δ^2*-Tetrahydroisophthalic Acid by Reduction of* iso*Phthalic Acid.*

By ERNEST HAROLD FARMER and HENRY LORIMER RICHARDSON.

IT was shown recently (Farmer and Richardson, J., 1926, 2173) that the Δ^2-tetrahydro*iso*phthalic acid of Perkin and Pickles (J., 1905, **87**, 293) does not possess glutaconic characteristics and should, on account of the ease with which it gives an anhydride and the nature of its oxidation products, be represented by the *cis*-Δ^4-formula. This correction quite precludes the possibility of a normal chemical relationship existing between the four tetrahydro-isomerides described by Perkin and Pickles: each of the possible ways of redistributing the formulæ involves a departure from customary chemical behaviour more serious than that connected with anhydride formation in the original scheme (below).



The most direct way of obtaining the necessary evidence for a reallotment of formulæ would appear to be oxidation of the remaining three isomerides. There are, however, two points which stand out from the evidence already recorded, and these have considerable importance in view of the later experimental results. The first concerns the conversion of the *cis*- into the *trans*-Δ^4-acid shown above; since the alleged *cis*-Δ^4-acid must have a structure other than that assigned to it in the scheme, the probability that the acid derived therefrom (by treatment with hydrochloric acid) is the *trans*-Δ^4-isomeride is greatly diminished. Secondly, the close similarity between the alleged Δ^3- and *trans*-Δ^4-acids and their similar behaviour on bromination strongly suggest their identity—a contingency which would reduce the number of isomerides isolated to three.

The main product of reduction of *iso*phthalic acid under the conditions described by Perkin and Pickles is the substance now regarded as the *cis*-Δ^4-acid (formerly Δ^2). Along with it appears a small quantity of an isomeric acid, m. p. 244° (Perkin and Pickles's Δ^3-acid): this is obviously not a primary product of reduction, since it is produced in still smaller quantity when the temperature and alkalinity during reduction are diminished; also it is produced quite readily by boiling the pure *cis*-Δ^4-acid with alkali. The constitution of this substance follows from its oxidation by ozone to β-carboxyadipic acid, and therefore the Δ^3-formula assigned to it by Perkin and Pickles is correct.

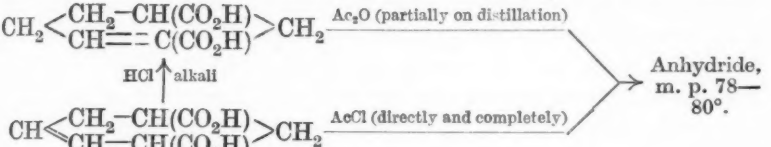
(II.) $\longrightarrow$ $\begin{matrix} HO_2C\cdot CH\cdot CH_2\cdot CO\cdot CO_2H \\ \quad\quad\quad\quad\quad\quad | \\ \quad\quad\quad\quad CH_2\cdot CH_2\cdot CO_2H \end{matrix}$ $\longrightarrow$ $\begin{matrix} HO_2C\cdot CH\cdot CH_2\cdot CO_2H \\ \quad\quad\quad\quad | \\ \quad\quad CH_2\cdot CH_2\cdot CO_2H \end{matrix}$

The second primary product of the reduction—regarded by Perkin and Pickles as the *cis*-Δ^4-acid—must, therefore, if it is a tetrahydro-*iso*phthalic acid, be either the true Δ^2- or the *trans*-Δ^4-form; both structures are difficult to reconcile with the recorded properties.

Considerable quantities of carefully purified *iso*phthalic acid have been reduced during these experiments, and the separation methods of Perkin and Pickles employed in isolating the products. We have been quite unable to satisfy ourselves that any portion of the reduction product contained a third isomeride. Not only has a third isomeride not been isolated, but oxidation of the entire residue after separation of the bulk of the pure Δ^3- and *cis*-Δ^4-acids has failed to yield any recognisable trace of adipic (or glutaric) acid.*

* Various portions approximating in melting point to that recorded for the "*cis*-Δ^4"-acid have been oxidised separately: one of these oxidations was referred to in a footnote of the previous memoir (p. 2173). Invariably the main product was tricarballylic acid.

The absence of the true Δ^2-acid from the reduction product therefore appears certain, and the remaining possibility, the occurrence of the *trans*-Δ^4-acid, is discounted on the following grounds: (1) non-isolability in the pure condition; (2) the inferior melting points of the residual portions of the reduction product; and (3) the strong indication afforded by the nature and analysis of the residues as to their consisting of mixtures of the Δ^3- and *cis*-Δ^4-acids with small quantities of non-isomeric impurities.* These results render the identity of Perkin and Pickles's Δ^3- and *trans*-Δ^4-forms all the more probable, and the relationship of the two veritable tetrahydro-acids, as represented below, is one which renders the direct conversion of the *cis*- into the *trans*-Δ^4-acid improbable of attainment.



It was noted by Perkin and Pickles that the dihydro*iso*phthalic acids appeared to be absent from their reduction products: this was the case also in our experiments. Yet the reduction may be regarded as normal in that it effects the hydrogenation of two CH:CH·CO groups. Further reduction experiments are being carried out and at the suggestion of Professor W. H. Perkin the synthesis of the Δ^2-tetrahydro-acid is being attempted.

Experimental.

Oxidation of Δ^3-Tetrahydroisophthalic Acid.—The acid, m. p. 243—244°, was prepared by boiling the *cis*-Δ^4-acid (Perkin and Pickles's Δ^2-acid) with 30% aqueous potash and recrystallising the product from water (with the aid of charcoal) and from formic acid. A solution of 5 g. of it in a slight deficit of aqueous sodium carbonate was treated with ozonised oxygen for 20 hours; the product, after being freed from ozone by a rapid stream of air, gave a strong, aldehydic reaction with Schiff's reagent and with ammoniacal silver nitrate, but yielded no semicarbazone. The precipitate of *iso*phthalic acid (0·25 g., identified as methyl ester) obtained on acidification was removed and the filtrate was neutralised with alkali and carefully treated with dilute permanganate solution at 0° until the latter was no longer reduced. From the mixture, worked up in the usual way, ether extracted about 4 g. of a crystalline acid,

* Nevertheless it has not been possible to demonstrate conclusively that the *trans*-Δ^4-acid is absent. It might quite well be produced in the reduction process and would yield tricarballylic acid on oxidation.

m. p. 110—115°; this, after recrystallisation from acetone–benzene and ethyl acetate, melted at 121° [Found: C, 44·3; H, 5·3; *M*(tribasic), 192. Calc. for $C_7H_{10}O_6$: C, 44·2; H, 5·3%; *M*, 190], alone or mixed with β-carboxyadipic acid prepared by Haworth and King's method (J., 1914, **105**, 1350).

Attempted Isolation of Perkin and Pickles's cis-Δ^4-*Acid.*—Since the Δ^2-acid of Perkin and Pickles is the true Δ^4-acid (almost certainly *cis*), the *cis*-Δ^4-acid of these authors must, if it represent a single isomeride of this series, be either the *trans*-Δ^4- or the Δ^2-form. On oxidation, the former of these should pass into tricarballylic acid, and the latter into adipic acid.

The earlier stages of Perkin and Pickles's calcium-salt method (*loc. cit.*, p. 302) for separating the reduction products of *iso*phthalic acid were followed. The calcium salt mother-liquors (the source of the "*cis*-Δ^4"-acid) yielded a glassy mass on evaporation. Fractional crystallisation of the acid regenerated from this (as described, *loc. cit.*, p. 311) yielded acid fractions of various melting points. Since samples approximating in m.p. to the recorded melting point "about 165°" * yielded considerable quantities of tricarballylic acid on oxidation with ozone, it was obvious that they did not consist of pure or nearly pure Δ^2-acid; the result, however, does not conflict with the Δ^4-structure for at least a portion of the material.

The acids obtained from a large quantity of the glassy calcium salts were regenerated and when solid were dissolved in hot water; almost pure Δ^3-acid separated on standing. The acids in the mother-liquor were reconverted into the calcium salts; a quantity of the less soluble calcium salt of the "Δ^2"-(true *cis*-Δ^4-)acid could then be removed. Again the mother-liquor yielded a glassy mass on evaporation. The alternate removal of Δ^3-acid and true *cis*-Δ^4-acid (as acid and calcium salt, respectively) was continued until less than 1 g. of acid (m. p. 165—200° after recrystallisation from formic acid) remained. This substance depressed the melting point of the pure *cis*-Δ^4-acid and gave very inferior analytical figures; it could not be regarded as a pure substance.

The acid material from the calcium salt mother-liquor appeared, therefore, to consist very largely of the Δ^3- and *cis*-Δ^4-acids. Of these, the former could readily be purified and identified beyond doubt; the purity of the latter, now free from all but the merest trace of the former, was not equally certain. Consequently, in

* The above authors state that the melting point must be regarded as approximate only, as the acid obviously may have contained traces of "Δ^2"-tetrahydro*iso*phthalic acid.

demonstrating the absence of the Δ^2-acid (below) this portion of the reduction product was included.

Absence of the Δ^2-Acid from the Reduction Products.—The whole of the acid products derived from the calcium salt mother-liquors, except that portion removed as pure Δ^3-acid (above), was dissolved in aqueous sodium carbonate and treated with ozone as described above. Ether extracted from the acidified solution a sticky solid, m. p. 163—169° after recrystallisation from formic acid. This substance (amounting to about one-third of the material taken), which appeared to be slightly impure *cis*-Δ^4-acid (m. p. 172°) that had escaped oxidation, was re-submitted to oxidation (below). The aqueous mother-liquor, which gave a strong aldehyde reaction, was carefully reoxidised with dilute permanganate solution at 0°. The manganese-free liquor therefrom was acidified and evaporated to dryness in a vacuum. Extraction of the residue with acetone yielded a gummy mass, an aqueous solution of which, on concentration, deposited crystals of tricarballylic acid, representing nearly one-half of the material taken. No trace of adipic or glutaric acid could be isolated from the small residue.

The unoxidised portion (above) was combined with the ethereal extract of all the mother-liquors and porous tiles likely to contain acid derived from the more soluble calcium salt, and the whole was oxidised as before. The ethereal extract of the acidified product was a gummy mass (representing about 45% of the material taken). This and the aqueous mother-liquor were separately oxidised with permanganate. The former yielded a very small quantity of *iso*phthalic acid and some acid material readily soluble in water; the latter also yielded readily soluble, acid material. From the combined water-soluble portions, on concentration, tricarballylic acid separated in considerable quantity. No trace of adipic or glutaric acid could be isolated from the residue. Thus, whilst there is no evidence of the presence of the true Δ^2-acid in these portions of the *iso*phthalic acid reduction product, it is possible, although improbable, that a portion of the tricarballylic acid was derived from the *trans*-Δ^4-acid.

The authors desire to express their thanks to the Chemical Society for a grant to one of them (H. L. R.) which has partly defrayed the cost of this research.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7. [*Received, December 2nd,* 1926.]

XI.—*The Rearrangement of the Alkylanilines.*

By Wilfred John Hickinbottom.

When an alkylaniline is heated in a sealed tube with hydrogen chloride (Hofmann and Martius, *Ber.*, 1871, **4**, 742) or certain metal chlorides (Reilly and Hickinbottom, J., 1920, **117**, 103) migration of the alkyl group from nitrogen to the nucleus occurs. This change has been regarded by Reilly and Hickinbottom as a true isomerisation and by Beckmann and Correns (*Ber.*, 1922, **55**, 852; compare also Howard and Derrick, *J. Amer. Chem. Soc.*, 1924, **46**, 166) as consequent to dissociation of alkyl halide from the alkylaniline hydrochloride.

If the latter assumption is correct, the formation of *p*-aminoalkylbenzene should be diminished or prevented under conditions which favour the removal of alkyl halide. It is necessary to select the conditions so that side reactions may be either detected or eliminated.

The behaviour of ethylaniline and butylaniline on heating in presence of metal chlorides in open tubes has been examined. If the rearrangement is due to the intermediate formation of alkyl chloride, either through the presence of traces of water (compare Chapman, J., 1925, **127**, 2818),

$$2NHR\cdot C_6H_5 + CdCl_2 + H_2O \longrightarrow 2RCl + 2C_6H_5\cdot NH_2 + CdO$$
$$\longrightarrow 2R\cdot C_6H_4\cdot NH_2 + CdCl_2 + H_2O,$$

or by exchange of halogen from metal to alkyl group, the product should contain a high proportion of aniline and a considerable quantity of metal or metal oxide. It is assumed that the reaction between the benzene nucleus and alkyl halide is not accelerated by metal chlorides. This assumption is supported by the observation that aluminium chloride or zinc chloride has no appreciable effect on the rearrangement of methylaniline hydrochloride (Beckmann and Correns, *loc. cit.*).

Butylaniline and ethylaniline, when heated in open tubes with the chloride of cobalt, cadmium, or manganese at 220—290°, gave *p*-aminobutyl- and *p*-aminoethyl-benzene, respectively. No alkyl chloride was detected during the reaction, and the yield of aniline was negligible. The rearrangement proceeded readily even when precautions were taken to exclude traces of moisture. When zinc chloride was used as a promoter, the principal product was *p*-aminoalkylbenzene; small quantities of aniline and more complex primary amines were also present.

To refute still further the view that the reaction may proceed according to the scheme given above, the behaviour of the alkylaniline hydrochlorides on being heated in open tubes was compared

with that of the free secondary amines in presence of metal chlorides under similar conditions. Ethylaniline hydrochloride, heated at 220—290° in open tubes, gave chiefly aniline, but also a small quantity of another primary amine. Dry butylaniline hydrochloride under similar conditions yielded *p*-amino-*n*-butylbenzene. The presence of small quantities of volatile impurities in the hydrochloride resulted in the production of aniline and *n*-butyl chloride.

The isomerisation of alkylanilines may be effected also by heating them in open tubes with metal salts other than chlorides.

Experimental.

In most of the experiments the amine hydrochloride or the mixture of amine and metallic salt was heated to the required temperature in a long, vertical test-tube. The volatile products could be collected when desired.

The secondary amines were carefully freed from traces of primary and tertiary amines.

Rearrangement of Alkylanilines in Presence of Metal Chlorides.

(a) *Formation of* p-*Aminoethylbenzene from Ethylaniline.*—(1) *In presence of cobalt chloride.* Dry ethylaniline (15 g.) and anhydrous cobalt chloride (7 g.), heated at 240—270° for 12 hours in a tube fitted with phosphoric oxide guard-tubes, yielded a solid, bluish-green mass of *p*-aminoethylbenzene cobaltochloride mixed with a small quantity of unchanged secondary amine. The pure cobaltochloride separated from methyl alcohol as a bright blue, crystalline mass.

In other experiments the ethylaniline was dried over fused potassium hydroxide or phosphoric oxide and distilled on to anhydrous cobalt chloride in an apparatus open to the air only through a train of phosphoric oxide tubes. The rearrangement under these conditions proceeded readily.

When cobalt chloride was used as a promoter a varying quantity of a grey, magnetic powder remained when the reaction product was dissolved in methyl alcohol (Found: Co, 96·8%. Found in the powder from another experiment in which the materials had not been dried: Co, 93·0%).

(2) *In presence of zinc chloride.* Ethylaniline (40 g.) was heated with half its weight of fused zinc chloride in a long-necked flask at 210° for 8 hours and finally for 2 hours at 260°. The product, triturated with an aqueous solution of zinc chloride and freed from the uncombined amine by washing with ether, yielded the primary amines as zincichlorides. Distillation of the free primary amines, followed by fractional crystallisation of the sulphates, furnished

pure *p*-aminoethylbenzene sulphate (14 g.) and a further quantity contaminated with aniline sulphate. There was a residue of amines of higher molecular weight.

p-Aminoethylbenzene was identified in the form of its acetyl derivative—slender needles from water, m. p. 95° (Beilstein and Kuhlberg, *Annalen*, 1870, 156, 208)—and its sulphate (Found: H_2SO_4, 28·4. Calc.: H_2SO_4, 28·8%). Replacement of the amino-group by chlorine and oxidation of the chlorohydrocarbon by alkaline permanganate yielded *p*-chlorobenzoic acid.

(b) *Formation of* p-*Amino*-n-*butylbenzene from* n-*Butylaniline.*—(1) *In presence of cobalt chloride.* A mixture of *n*-butylaniline and cobalt chloride, maintained at 230—240° for 15 hours, gave a product consisting of *p*-amino-*n*-butylbenzene and some unchanged secondary amine. No butyl chloride was detected.

(2) *In presence of zinc chloride.* Butylaniline (35 g.) and zinc chloride (19 g.), heated at 220—230° for 11 hours, yielded *p*-amino-*n*-butylbenzene (18 g.), impure aniline (1·8 g.), primary amines of higher molecular weight (4·5 g.), and secondary amines (8 g.).

(3) *In presence of manganese chloride.* The product after 15 hours' heating at 240—250° contained approximately 30% of *p*-amino-*n*-butylbenzene. No appreciable quantity of other primary amines was present.

(4) *In presence of cadmium chloride.* Dry butylaniline and anhydrous cadmium chloride, heated at 190° for 4 hours and then at 250—290° for 14 hours, gave *p*-amino-*n*-butylbenzene cadmichloride, some secondary amine, and a trace of a tertiary amine.

p-Amino-*n*-butylbenzene was isolated from the reaction mixture usually through its insoluble zincichloride, and was freed from other primary amines by fractional crystallisation of its sulphate. It was identified by comparison of its benzenesulphonyl derivative, m. p. 78°, and acetyl derivative with authentic specimens.

Behaviour of Alkylaniline Hydrochlorides on Heating.

Ethylaniline Hydrochloride.—The dry hydrochloride, heated in an open tube at 200—220° for 15 hours, gave a pale yellow, soft, crystalline mass (Found: Cl, 15·7%) consisting of a mixture of primary and secondary amines with a small quantity of diethylaniline. The primary amines comprised aniline (80% was isolated in a pure state), and another amine not definitely identified. In many other experiments, the principal product was aniline, although the temperature and duration of heating were varied considerably.

Butylaniline Hydrochloride.—No butyl chloride was obtained when the dry hydrochloride was heated at 230—235° for 18 hours. The product was *p*-amino-*n*-butylbenzene and a small quantity of aniline.

The presence of free hydrogen chloride or of benzene in the hydrochloride led to the isolation of *n*-butyl chloride (6·2 c.c. from 23 g. of hydrochloride in one experiment); the residual amines contained chiefly aniline, some *n*-butylaniline, and another primary amine in small quantity.

Rearrangement of Alkylanilines in Presence of Sulphates and Phosphates.

Silver Sulphate.—Ethylaniline (6 g.) and silver sulphate (2 g.), maintained at 200—230° for 16 hours, gave a dark brown, viscous mass having the odour of hydrogen sulphide and containing embedded in it a cake of silver sulphide with some silver sulphate (Found: Ag, 89·3; S, 6·4%). Extraction with alcohol, evaporation of the alcoholic solution with dilute hydrochloric acid, and filtration to remove tarry material yielded a solution from which *p*-aminoethylbenzene was isolated through its zincichloride and sulphate. Other primary amines, more complex than *p*-aminoethylbenzene, were also present, but were not isolated in a pure state.

Butylaniline, heated with silver sulphate under similar conditions, yielded *p*-amino-*n*-butylbenzene. A considerable proportion of more complex and amorphous products was present. The yield of pure sulphate was usually 0·2 g. from 5 g. of secondary amine. Prolonged heating reduced the yield of primary amine.

Anhydrous copper sulphate, heated with *n*-butylaniline at 200—250°, gave a dense black tar from which a primary amine was isolated as a sparingly soluble sulphate, but the yield was so small that the reaction was not further examined.

Copper Phosphate.—Ethylaniline (5 g.), heated with copper phosphate (2 g.) at 250° for 14 hours, yielded *p*-aminoethylbenzene, metallic copper (Cu, 98·6%), and metaphosphoric acid.

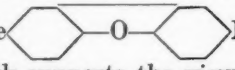
UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

[*Received, June 15th*, 1926.]

XII.—*Substituted Diaryl Ethers. Part I. Di-p-tolyl Ether.*

By JOSEPH REILLY, PETER J. DRUMM, and HERBERT S. BOYD BARRETT.

WHILST the mixed ethers such as anisole and phenetole have been extensively studied, the substituted diaryl ethers derived from alkylphenols have received scarcely any attention, although from the newer aspects of chemical theory their reactions and the orientation of their derivatives are of interest.

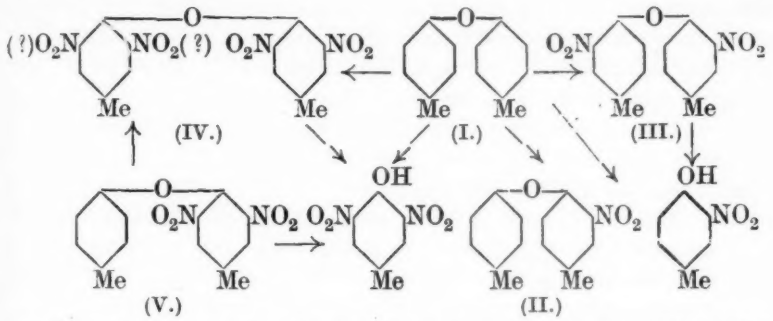
Di-*p*-tolyl ether was selected as typical of the class of substances indicated. The only two references to this compound in the literature are the following : Busch (*Ber.*, 1884, **17**, 2638) claimed to have prepared ditolyl ether by heating *p*-cresol with zinc chloride to 300° and gave the melting point as 165°, whilst Gladstone and Tribe (J., 1882, **41**, 9), by distilling aluminium *p*-tolyloxide, isolated, in small amounts, a substance of m. p. 50° which, from analogy with diphenyl ether, they called *p*-cresyl ether. In the present work, di-*p*-tolyl ether (I) was prepared in very good yield from *p*-cresol and *p*-bromotoluene, and the work of Gladstone and Tribe confirmed. Sabatier and Mailhe (*Compt. rend.*, 1910, **151**, 494), by the catalytic dehydration of *p*-cresol with thoria at 470°, obtained a compound similar to that of Busch to which they assigned the constitution  , *i.e.*, di-*p*-tolylene ether. The present work supports the views of Sabatier and Mailhe. It would appear, therefore, that the only authentic reference in the literature to di-*p*-tolyl ether is that of Gladstone and Tribe (*loc. cit.*).

Di-*p*-tolyl ether behaves normally on oxidation, forming an ether acid which on distillation with soda-lime gives phenol and diphenyl ether.

Di-*p*-tolyl ether condenses with acetyl and benzoyl chlorides and phthalic anhydride in the presence of aluminium chloride to give monoketonic and not diketonic derivatives as might be expected. These develop characteristic colours with sulphuric acid, accompanied by fluorescence in the case of the last two compounds. These compounds behave abnormally with phenylhydrazine and hydroxylamine and will form the subject of a further communication.

The behaviour of di-*p*-tolyl ether on nitration is in many ways different from that of diphenyl ether and hitherto no nitration products of this substance have been described. Diphenyl ether nitrates smoothly to nitrodiphenyl ethers with very little decomposition to nitrophenols (Ryan and Drumm, *Proc. Roy. Soc. Dublin*, 1924, **17**, 313). Di-*p*-tolyl ether, on the other hand, under the different conditions of nitration described below, gave mono- and dinitro-*p*-cresols as the main product, the nature of the by-product, consisting of small quantities of various nitrodi-*p*-tolyl ethers, depending on the experimental conditions. Amongst the new nitro-products isolated and identified by synthesis were 2-*nitrodi*-p-*tolyl ether* (II), 2 : 2′-*dinitrodi*-p-*tolyl ether* (III), and a tetranitro-compound which is probably 2 : 6 : 2′ : 6′-*tetranitrodi*-p-*tolyl ether* (IV). 2 : 6-Dinitrodi-*p*-tolyl ether (V) was obtained by the condensation of *p*-cresol with 3 : 5-dinitro-*p*-bromotoluene. In addition, 3-nitro- and 3 : 5-dinitro-*p*-cresols were isolated in certain

cases. The actual scheme of nitration may be indicated as follows :



2-Nitrodi-*p*-tolyl ether is readily reduced to 2-aminodi-*p*-tolyl ether, and the latter diazotises and gives azo-dyes. These substances, together with the amino-compounds from the other nitro-derivatives of di-*p*-tolyl ether, are being further examined.

EXPERIMENTAL.

*Di-*p*-tolyl Ether.*—In the preliminary experiments, *p*-cresol, *p*-bromotoluene, powdered potassium hydroxide, and a trace of copper bronze were heated at 200—250° for 3 to 4 hours, the procedure used in the case of diphenyl ether being followed. The product, on distillation in steam, gave much unchanged bromotoluene, followed by a small quantity of oil, which solidified (yield, 20—25%). By altering the method as follows, the yield was increased to 87%. Potassium *p*-tolyloxide (dried at 150° in a vacuum) (35 g.), *p*-bromotoluene (commercial *p*-bromotoluene purified by standing in contact with sulphuric acid to remove traces of isomerides; m. p. of purified product, 28·5°) (41 g.), copper bronze (Naturkupfer C; washed with ether to remove oily impurities) (0·3 g.), and *p*-cresol (20 g.) (solvent) were slowly heated in a dried flask fitted with an air condenser. Reaction commenced at 200°, with separation of potassium bromide. The heating was continued for 2 hours at 230—240°. The dark product was made alkaline with aqueous potassium hydroxide and distilled in steam. Unchanged bromotoluene passed over, followed by an oil which quickly solidified; this crystallised from ethyl alcohol in colourless prisms, m. p. 50° (Found : C, 84·5; H, 7·3; *M*, cryoscopic in naphthalene, 191. Calc. for $C_{14}H_{14}O$: C, 84·8; H, 7·1%; *M*, 198).

Di-*p*-tolyl ether is very soluble in acetone, ether, or benzene, readily soluble in hot alcohol or warm glacial acetic acid, and insoluble in water. It has a pleasant odour, similar to, but fainter than, that of diphenyl ether.

Di-p-*tolylene Oxide.*—*p*-Cresol (25 g.) and litharge (50 g.) were intimately mixed and heated (oil-bath) at 110—120° for 10 hours. The product, after cooling, was powdered and distilled. At first, unchanged *p*-cresol passed over. The fraction, b. p. above 300°, set to a crystalline solid and separated from boiling light petroleum (b. p. 70—100°) in glistening, pearly plates, m. p. 165°. Prepared in a manner analogous to that of diphenylene oxide from phenol, this substance is obviously di-*p*-tolylene oxide. Its further investigation is in progress.

Oxidation of Di-p-*tolyl Ether.*—A solution of chromic acid in glacial acetic acid was gradually added, with stirring, to an acetic acid solution of di-*p*-tolyl ether at 40° until oxidation was apparently completed. The gelatinous precipitate that formed on dilution with water was separated from the liquid by the streamline filter, washed with water, and repeatedly dissolved in aqueous ammonia and precipitated with hydrochloric acid. The collected solid was converted into the silver salt in the usual manner (Found: Ag, 45·4. $C_{14}H_8O_5Ag_2$ requires Ag, 45·7%). Di-*p*-carboxydiphenyl ether is a white, amorphous solid which does not melt. It is easily soluble in alkalis and is precipitated therefrom by acids. The silver salt, sparingly soluble in water, is readily soluble in ammonia.

An intimate mixture of the above acid (1 part) with dry soda-lime (4 parts) was strongly heated in a retort. The small amount of oil, smelling strongly of phenol, that distilled was extracted with ether, and the ethereal layer well washed with aqueous sodium hydroxide to remove phenolic substances. On evaporation of the ether an oil remained which gradually solidified in a freezing mixture. This substance, m. p. 28°, was identified as diphenyl ether by the method of mixed melting point.

Action of Nitric Acid on Di-p-*tolyl Ether under Various Conditions.*—*In acetic acid solution.* To a well-cooled solution of nitric acid (12 c.c.; *d* 1·5) in glacial acetic acid (50 c.c.), di-*p*-tolyl ether (5 g.) was slowly added, with constant stirring. The temperature was allowed to rise slowly to 30°, and the red solution was then poured on to crushed ice. The precipitated yellow oil in ethereal solution was washed with dilute potassium hydroxide solution and with water and dried. The residual oil, cooled in a freezing mixture, set to a crystalline solid (2 g.) which was dried on a porous tile and crystallised from ethyl alcohol, colourless prisms, m. p. 50°, being obtained (Found: N, 5·6. $C_{14}H_{13}O_3N$ requires N, 5·7%). This substance (A) is therefore one of the mononitro-derivatives of di-*p*-tolyl ether and its constitution was determined later by direct synthesis. The dark red potash extract was acidified with dilute

hydrochloric acid, and the yellow precipitate collected and distilled in steam. From the distillate a yellow solid separated (1 g.). This, after crystallisation from dilute aqueous ethyl alcohol, melted at 33° and showed no depression of melting point when mixed with 3-nitro-*p*-cresol. From the residue after distillation was isolated a crystalline substance (2 g.), m. p. 85°, which was identified as 3 : 5-dinitro-*p*-cresol by the mixed melting-point method.

Direct nitration. Cold nitric acid of concentrations up to *d* 1·4 is without appreciable action on di-*p*-tolyl ether. On heating the mixture a very vigorous reaction, which was difficult to control, commenced at 70°, with copious evolution of nitrous fumes. With nitric acid of a higher density, under the following conditions, a dinitrodi-*p*-tolyl ether was isolated. Di-*p*-tolyl ether (5·5 g.) was added during 1 hour to nitric acid (10 c.c.; *d* 1·5) at −10° to −5°. In the absence of very efficient external cooling the reaction tends to become rather violent. The resulting dark red solution was poured on to crushed ice. The precipitated oily solid was washed in ethereal solution with dilute aqueous sodium hydroxide, until this showed no coloration, then with water, and dried. The residue from the ethereal solution was re-extracted with light petroleum (b. p. 70—100°). From the latter, a yellow substance (B) (1 g.) slowly separated which crystallised from alcohol in slender plates, m. p. 126° (Found : N, 9·9. $C_{14}H_{12}O_5N_2$ requires N, 9·7%). The constitution of this dinitrodi-*p*-tolyl ether was determined later by direct synthesis. From the alkaline extract 3 : 5-dinitro-*p*-cresol (4 g.) was isolated in the usual way.

With a mixture of sulphuric and nitric acids. Finely powdered di-*p*-tolyl ether (5 g.) was added slowly to a mixture of 98% sulphuric acid (25 g.) and nitric acid (25 g.; *d* 1·5) at −10° with thorough stirring and cooling in a freezing mixture. The resulting highly-coloured solution was poured on to crushed ice. The precipitated light brown oil was extracted with ether, and the ether extract freed from nitrocresols in the usual way. From the ether was obtained a yellow solid (1 g.) which was separated into two fractions by means of boiling light petroleum (b. p. 70—100°); the soluble part consisted of a dinitrodi-*p*-tolyl ether identical with that obtained by direct nitration; the insoluble portion (C) separated from boiling ethyl alcohol in colourless, rectangular plates, m. p. 246° (Found : N, 14·6. $C_{14}H_{10}O_9N_4$ requires N, 14·8%). This analysis agrees with that for a tetranitrodi-*p*-tolyl ether and the orientation of two of the nitro-groups has been ascertained as described later.

*Action of Gaseous Nitrogen Peroxide on Di-*p*-tolyl Ether.*—Dry liquid nitrogen peroxide, prepared from dry lead nitrate, and di-*p*-

tolyl ether were placed in two shallow containers left side by side under a bell-jar. Initially the absorption of the nitrogen peroxide was rapid and it needed renewal from time to time. The tolyl ether lost its crystalline form and after a week appeared as an intumescent, brown syrup. The method of working up employed was the same as that for the products of direct nitration. From it was isolated, in addition to 3 : 5-dinitro-*p*-cresol, a dinitrodi-*p*-tolyl ether (1·2 g.), m. p. 126°, identical in every respect with the dinitro-product obtained by direct nitration.

Syntheses of Nitrodi-p-*tolyl Ethers.* — *2-Nitrodi*-p-*tolyl ether.* Potassium *p*-tolyloxide (7 g., dried at 150° in a vacuum), 4-bromo-3-nitrotoluene (9 g.), copper bronze (0·1 g.), and *p*-cresol (20 g.) (solvent) were slowly heated (oil-bath), with stirring, in a flask fitted with an air condenser. At 160°, reaction set in with separation of potassium bromide. Heating was continued for 3 hours at 210—220°. The dark product was extracted with ether and the ethereal layer was washed with dilute sodium hydroxide solution until the latter was colourless, and then with water. On fractionation of the dried ethereal extract under diminished pressure, a pale yellow oil (3 g.) distilled at 220°/15 mm. The oil solidified to a mass of light yellow crystals, m. p. 46—48°, and separated from alcohol in colourless prisms, m. p. 50° (Found : N, 5·6. $C_{14}H_{13}O_3N$ requires N, 5·7%). 2-Nitrodi-*p*-tolyl ether is freely soluble in benzene, ether, or chloroform, and less soluble in light petroleum (b. p. 70—100°) or ethyl alcohol. It is not hydrolysed by boiling with potassium hydroxide solution (20%), as evidenced by the negligible amount of colour developed in solution after 10 hours. The nitro-group was reduced by tin and hydrochloric acid; the resulting amino-compound diazotised and then coupled with alkaline β-naphthol to give a scarlet azo-dye. 2-Nitrodi-*p*-tolyl ether agrees in every respect, including mixed melting point, with the mononitro-derivative (A) obtained by nitration, in acetic acid solution, of di-*p*-tolyl ether.

2 : 2′-*Dinitrodi*-p-*tolyl ether.* Potassium 3-nitro-*p*-tolyloxide (6 g., dried at 100° in a vacuum), 4-bromo-3-nitrotoluene (6 g., prepared by diazotisation in dilute sulphuric acid of 3-nitro-*p*-toluidine with subsequent conversion into the diazonium perbromide and decomposition of this with a small amount of absolute ethyl alcohol), 3-nitro-*p*-cresol (15 g.) (solvent) and copper bronze (0·2 g.) were heated (oil-bath), with stirring, very slowly to 190°, and then, after 1 hour, to 210° during 3 hours. The highly coloured product was powdered and repeatedly extracted with ether, and the ethereal layer was freed from nitrocresol in the usual way. The residue left after removal of the ether was extracted with boiling light petroleum

(b. p. 70—100°), from which a yellow, crystalline solid slowly separated. This solid crystallised from ethyl alcohol in pale yellow, slender laminæ, m. p. 126° (Found : N, 9·9. $C_{14}H_{12}O_5N_2$ requires N, 9·7%).

2 : 2′-Dinitrodi-*p*-tolyl ether is colourless when pure, but gradually assumes a yellow colour in contact with air. It is very soluble in ether or benzene and readily soluble in hot light petroleum (b. p. 70—100°) or hot ethyl alcohol. It is slowly hydrolysed by boiling potassium hydroxide solution (20%), more readily by alcoholic potassium hydroxide, with formation of 3-nitro-*p*-cresol. It is identical with the dinitro-derivative (B) obtained by direct nitration of di-*p*-tolyl ether.

2 : 6-*Dinitrodi*-p-*tolyl ether*. Potassium *p*-tolyloxide (6 g.) and 3 : 5-dinitro-*p*-bromotoluene (prepared by the method of Jackson and Ittner, *J. Amer. Chem. Soc.*, 1897, **19**, 7) (7·5 g.) were heated in alcoholic solution on the steam-bath for 4 hours. The solution became orange-coloured and potassium bromide separated almost immediately. The solution was filtered hot and, on cooling, deposited faintly yellow crystals, m. p. 98—100°. The pure substance was obtained from alcohol in colourless, slender prisms, m. p. 107° (Found : N, 9·9. $C_{14}H_{12}O_5N_2$ requires N, 9·7%).

2 : 6-Dinitrodi-*p*-tolyl ether is easily soluble in ether, chloroform, or acetone and sparingly soluble in cold ethyl alcohol or cold light petroleum. It is readily hydrolysed by boiling alcoholic potassium hydroxide with formation of *p*-cresol and 3 : 5-dinitro-*p*-cresol. In contact with air, it gradually assumes a yellow colour.

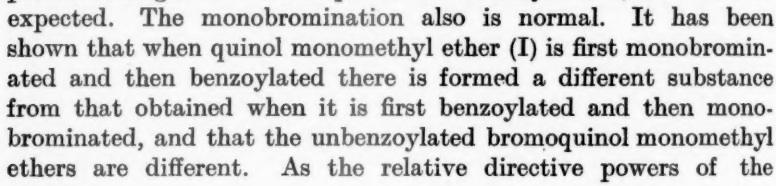
Nitration of 2 : 6-*Dinitrodi*-p-*tolyl Ether*.—To nitric acid (12 c.c.; *d* 1·5) was slowly added 2 : 6-dinitrodi-*p*-tolyl ether (2·6 g.), the temperature being maintained at −5°. The solution was then poured on to ice, and the yellow precipitate freed from small amounts of nitrocresols as before. The residue crystallised from glacial acetic acid in colourless plates, m. p. 246° (Found : N, 14·6. $C_{14}H_{10}O_9N_4$ requires N, 14·8%). The tetranitrodi-*p*-tolyl ether is freely soluble in acetone, much less soluble in ether, chloroform, or benzene, and practically insoluble in cold glacial acetic acid or light petroleum. It is readily hydrolysed by hot alcoholic potassium hydroxide with formation of 3 : 5-dinitro-*p*-cresol. It agrees in melting point and other properties with the tetranitro-compound (C) obtained by the nitration of di-*p*-tolyl ether in a mixture of nitric and sulphuric acids.

UNIVERSITY COLLEGE, CORK. [*Received, September* 24*th*, 1926.]

XIII.—*Bromination of Quinol Monomethyl Ether.*

By Frank Mouat Irvine and John Charles Smith.

Contrary to the statement by Kohn and Guttmann (*Monatsh.*, 1924, **45**, 575) that dibromination of quinol monomethyl ether yields only the 2 : 5-dibromoquinol monomethyl ether, it has been proved that only 30—35% of this isomeride is formed, the main product being 2 : 6-dibromoquinol monomethyl ether, as would be expected. The monobromination also is normal. It has been shown that when quinol monomethyl ether (I) is first monobrominated and then benzoylated there is formed a different substance from that obtained when it is first benzoylated and then monobrominated, and that the unbenzoylated bromoquinol monomethyl ethers are different. As the relative directive powers of the



hydroxy-, methoxy-, and benzoyloxy-groups are in the order OH > OMe > OBz, these two bromophenols must be 2-*bromoquinol monomethyl ether* (II) and 3-*bromoquinol monomethyl ether* (VI), and the corresponding benzoyl derivatives must be represented by (III) and (V), respectively.

Experimental.

2-*Bromoquinol Monomethyl Ether* (II).—Quinol monomethyl ether (m. p. 53°, entirely free from quinol; compare Robinson and Smith, J., 1926, 393) gave a homogeneous monobromination product on treatment with excess of bromine in carbon disulphide solution.

To a solution of the quinol monomethyl ether (6·2 g.; 1 mol.) in cold carbon disulphide (140 c.c.) was slowly added, with stirring, a 20% (vol.) solution of bromine in carbon disulphide (12·5 c.c.; 1 mol.). When the yellow colour had almost disappeared, the solvent was distilled off. The residue, which solidified (m. p. 40—42°; yield, almost theoretical), was quickly recrystallised from ligroin (b. p. 60—80°) and obtained as long, colourless needles, m. p. 44—45° (Found : C, 41·5; H, 3·6. $C_7H_7O_2Br$ requires C, 41·4; H, 3·5%). The acetyl derivative was a liquid, but the *benzoyl* derivative (III), obtained in 95% yield by the Schotten-Baumann method, when recrystallised from ligroin (b. p. 80—100°), melted sharply at 85°

(Found : C, 54·8; H, 3·6; Br, 26·0. $C_{14}H_{11}O_3Br$ requires C, 54·7; H, 3·6; Br, 26·0%).

3-*Bromoquinol Monomethyl Ether* (VI).—4-*Methoxyphenyl benzoate* (IV), obtained by the Schotten-Baumann method, melted sharply at 87°, but required recrystallisation from alcohol and from ligroin before it was pure enough for analysis (Found : C, 73·6; H, 5·4. $C_{14}H_{12}O_3$ requires C, 73·7; H, 5·3%). It could be brominated in warm acetic acid solution with an iron catalyst, or in anhydrous formic acid. The solid (11·4 g.; 1 mol.), dissolved in formic acid (75 c.c.), was warmed on a steam-bath while a solution of bromine (3·0 c.c.; 1·2 mols.) in an equal volume of formic acid was run in dropwise; the mixture was gently boiled for a few minutes until the excess of bromine was driven off, then poured into water (500 c.c.); the brown oil which formed rapidly solidified (16·1 g.). On recrystallisation from alcohol, pure 3-*bromo*-4-*methoxyphenyl benzoate* (V), white needles, m. p. 105·5°, was obtained (Found : C, 54·8; H, 3·6. $C_{14}H_{11}O_3Br$ requires C, 54·7; H, 3·6%). After hydrolysis with aqueous methyl-alcoholic sodium hydroxide, pure benzoic acid and a bromophenol (theoretical yields) were separated by means of sodium bicarbonate solution. Recrystallisation from a small volume of benzene gave long prisms, m. p. 77—78°, of 3-*bromoquinol monomethyl ether* (VI) (Found : C, 41·2; H, 3·5; Br, 39·5. $C_7H_7O_2Br$ requires C, 41·4; H, 3·5; Br, 39·4%).

2 : 6-*Dibromoquinol Dimethyl Ether*.—In the method of preparation given by Kohn and Guttmann (*loc. cit.*, p. 582), the following improvements were introduced. Tribromophenol bromide (m. p. 137—141°), obtained from phenol (1 g. in 750 c.c. of water) and excess of bromine water, was recrystallised from warm (40°) chloroform and found always to melt at 140—141° (decomp.) [Found : Br (by potassium iodide), 38·7. Calc. : Br, 39·0%]. It was found unnecessary to extract the crude tribromophenol bromide with alkali as recommended by Auwers and Büttner (*Annalen*, 1898, **302**, 141). 2 : 6-Dibromobenzoquinone (m. p. 132°), prepared from tribromophenol bromide and fuming nitric acid, was reduced in aqueous suspension by means of sulphur dioxide to 2 : 6-dibromoquinol; a quantitative yield was obtained by carrying out the reduction in the cold until the red colour first produced had almost disappeared (10 minutes) and then gradually warming the mixture to 100°. Methylations of 2 : 6-dibromoquinol (m. p. 162—163°) with sodium or potassium hydroxide solution and pure methyl sulphate gave crude products, m. p. 37—38° (yields, 70—85%); these, after recrystallisation from methyl or ethyl alcohol, formed almost regular hexagonal plates, m. p. 38—39°. Some days later, the crystals had changed to elongated hexagonal plates, the m. p.,

53°, of which was unaltered by further recrystallisation (Found: C, 32·3; H, 2·7; Br, 53·8. Calc.: C, 32·4; H, 2·7; Br, 54·0%). The crystals melting at 53° are exactly like those described and measured by Kohn and Guttmann but stated by them to melt at 56°.

Dibromination of Quinol Monomethyl Ether.—In every case, the dibromination of the quinol monomethyl ether (6·2 g.; 1 mol.) was performed at 10° in well-stirred glacial acetic acid solution (30 c.c.) by slowly adding bromine (5 c.c.; 2 mols.) in acetic acid (15 c.c.). A clean product * was obtained by distilling the hydrobromic and acetic acids during ¾ hour at 30—40°/5—10 mm. in a slow current of dry air drawn through the liquid. The residue (14·0 g.; quantitative yield) soon set to a pink, crystalline mass, m. p. 60—80°. It could be recrystallised from dilute acetic acid or from hexane; but the best method of separation was that of Kohn and Guttmann, by methylation, 2 : 5-dibromoquinol dimethyl ether (Habermann, *Ber.*, 1878, **11**, 1034) being insoluble in cold alcohol. Kohn and Guttmann, however, failed to realise that the easily soluble 2 : 6-dibromoquinol dimethyl ether might be present in the alcoholic mother-liquor.

In a test experiment, a mixture of 2 : 5-dibromoquinol dimethyl ether (m. p. 144—145°; 1·0 g.) and the 2 : 6-isomeride (1·0 g.) was recrystallised from alcohol and gave a first crop of 0·94 g., m. p. 142—143°. Complete evaporation of the mother-liquor left 1·02 g. of crystals, m. p. 45—48°, from which by repeated recrystallisation 0·2 g. of the pure 2 : 6-isomeride, m. p. 53°, was obtained. When 1·0 g. of the soft, colourless, crystalline mixture (m. p. 43—130°) from the methylation of some dibromination product (recrystallised from hexane) was recrystallised from alcohol, only 0·4 g. of 2 : 5-dibromoquinol dimethyl ether (m. p. 142—143·5°) was obtained. After complete evaporation of the mother-liquor, clusters of well-formed, elongated hexagonal plates (0·55 g.) remained, m. p. 45—50°. Repeated crystallisation from alcohol raised the m. p. to 51—53° (Found: Br, 53·9. Calc.: Br, 54·0%). The mixed melting point with a specimen of 2 : 6-dibromoquinol dimethyl ether, m. p. 53°, was 52—53°.

In order to obtain a more accurate analysis, experiments were performed in which the entire yields of the crude bromination products were methylated, and the dimethyl ethers isolated by extraction with ether. Losses in methylation would probably be heavier in the case of the diortho-substituted 2 : 6-isomeride, so that

* The addition of ice-water to the stirred reaction mixture at first precipitates a cream-coloured oil, but the colour suddenly turns reddish-brown and then black, large amounts of tar being formed.

the proportion of 2 : 5-dibrominated product found would be a maximum. It is possible also that some 2 : 3-dibromoquinol dimethyl ether (a compound not yet known) was formed. In two experiments, 6·2 g. of quinol monomethyl ether gave 12·85 g. (yield, 87%) and 11·70 g. (yield, 79%), respectively, of mixed dibromoquinol dimethyl ethers; the quantities of the 2 : 5-isomeride isolated were 4·30 g. (yield, 33·5%) and 3·65 g. (yield, 31·2%), respectively.

Summary.

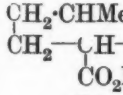
Quinol monomethyl ether yields on monobromination *2-bromoquinol monomethyl ether*, and on dibromination not more than 30—35% of 2 : 5-dibromoquinol monomethyl ether, the remainder being mostly 2 : 6-dibromoquinol monomethyl ether. *3-Bromoquinol monomethyl ether* also is described.

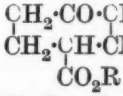
THE UNIVERSITY, MANCHESTER. [*Received, November 6th,* 1926.]

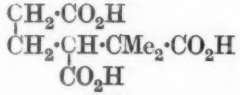
XIV.—*The Constitution of the Acid formed by the Action of Sulphuric Acid on Camphorquinone.*

By MADHAV BALAJI BHAGVAT and JOHN LIONEL SIMONSEN.

IN a recent communication (J., 1925, **127**, 1294), evidence was advanced which appeared to prove that the keto-acid, $C_{10}H_{16}O_3$, first prepared by Manasse and Samuel (*Ber.*, 1897, **30**, 3157; 1902, **35**, 3831) by the action of sulphuric acid on camphorquinone, was *d*-2 : 2 : 4-trimethyl*cyclo*hexan-3-one-1-carboxylic acid (I). The assignment of this constitution to the acid was based essentially on two facts: (i) on oxidation with nitric acid it gave β-methylpentane-βγε-tricarboxylic acid (III), and (ii) on treatment with amyl nitrite and hydrochloric acid it did not yield an oximino-derivative, the formation of which might have been expected if the keto-acid had the alternative constitution (II) (compare footnote, *loc. cit.*, p. 1295), since in this case there is a methylene group adjacent to the carbonyl group.


(I.)


(II.; R = H, Me.)


(III.)

In deciding between these two formulæ, owing to the symmetry of the molecules, simple degradation products were unlikely to be of much assistance, but it seemed probable that, on bromination, a dibromo-acid would result of either formula (IV) or (V). It was

further anticipated that this acid would, on removal of two molecules of hydrogen bromide, tend to lose simultaneously a methyl group and so pass into a phenolic acid (VI or VII) the identification of which would have offered little difficulty.

(IV.) $\begin{matrix}CH_2—CBrMe—CO\\ CH_2\cdot CBr(CO_2H)\cdot CMe_2\end{matrix}$ $\qquad$ $\begin{matrix}CHBr—CO—CHMe\\ CH_2\cdot CBr(CO_2H)\cdot CMe_2\end{matrix}$ (V.)

(VI.) $\begin{matrix}CH{=}CMe—C\cdot OH\\ CH{:}C(CO_2H)\cdot CMe\end{matrix}$ $\qquad$ $\begin{matrix}CH{=}C(OH)—CMe\\ CH{:}C(CO_2H)\cdot CMe\end{matrix}$ (VII.)

On bromination in acetic acid, the crystalline and the liquid methyl ester of the keto-acid each gave a *dibromo*-ester, $C_{11}H_{16}O_3Br_2$, which reacted in an identical manner with alkali. In some experiments, under conditions which could not be exactly defined, the dibromo-ester was obtained crystalline. Since both the pure crystalline ester and the crude liquid ester yielded the same products, they were apparently stereoisomerides.

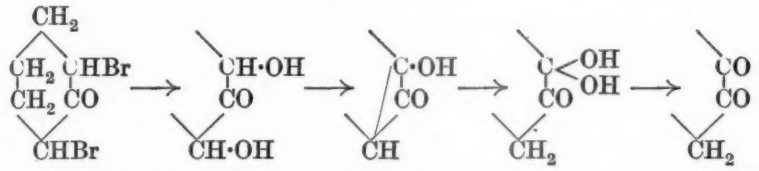
On treatment with a solution of barium or potassium hydroxide the dibromo-ester gave a complex mixture of acids, from which, with considerable difficulty, (A) a *hydroxyketo-acid*, $C_{10}H_{14}O_4$, m. p. 151—152°, (B) a dibasic *hydroxy-acid*, $C_{10}H_{16}O_5$, m. p. 191—192°, (C) and (D) unsaturated dibasic *acids*, $C_{10}H_{14}O_4$, m. p. 257° and 215—216°, respectively, were isolated.

The formation of the hydroxyketo-acid, which also reacted as a diketo-acid, yielding a *dioxime* and a *disemicarbazone*, would appear to indicate that the dibromo-ester has two bromine atoms attached to the same carbon atom—a fact most simply explained if the original keto-ester has formula (II), the dibromo-ester then being represented by (VIII). An ester of this formula should yield on treatment with alkali a diketo-acid (IX); the acid obtained, however, and also its *methyl* ester, were colourless substances which gave intense colorations with ferric chloride, and the methyl ester was readily soluble in dilute potassium hydroxide solution and reprecipitated by carbon dioxide. Moreover, in alkaline solution, the acid was unstable to potassium permanganate and on treatment with acetyl chloride it yielded an *acetyl* derivative. There can be no doubt, therefore, that the hydroxyketo-acid is represented by (X) or (XI), the latter being the more probable, since the acid shows no tendency to yield a lactone. Owing to the small quantity of material available, the decision between these two formulæ could not be made.

(VIII.) $\begin{matrix}CBr_2—CO—CHMe\\ CH_2\cdot CH(CO_2Me)\cdot CMe_2\end{matrix}$ $\qquad$ $\begin{matrix}CO—CO—CHMe\\ CH_2\cdot CH(CO_2H)\cdot CMe_2\end{matrix}$ (IX.)

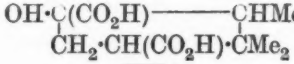
(X.) $\begin{matrix}C(OH)—CO—CHMe\\ CH\cdot CH(CO_2H)\cdot CMe_2\end{matrix}$ $\qquad$ $\begin{matrix}CO—C(OH){=}CMe\\ CH_2\cdot CH(CO_2H)\cdot CMe_2\end{matrix}$ (XI.)

In its general properties this acid resembles the diketones or, more correctly, the hydroxy-ketones obtained by Wallach (*Annalen*, 1918, **414**, 296) in an analogous manner by the action of alkali on the dibromo-derivatives of various cyclic ketones. Wallach considered that the two bromine atoms were not attached to the same carbon atom and that the formation of the diketone proceeded in accordance with the scheme :

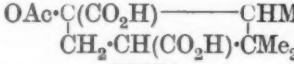


Our experiments do not furnish any evidence in support of this somewhat complicated series of reactions and we prefer for the present to assume that the dibromo-ester has formula (VIII).

The hydroxyketo-ester (or acid), on digestion with a strong solution of potassium hydroxide (50% KOH), behaves in a similar manner to Wallach's hydroxy-ketones, undergoing molecular rearrangement with addition of water and becoming converted into a dibasic hydroxy-acid identical with the acid (B) that forms the main product of the action of alkali on the dibromo-ester. There can be no doubt that this acid is 1-*hydroxy*-4 : 4 : 5-*trimethyl*cyclo*pentane*-1 : 3-*dicarboxylic acid* (XII). It yields an unsaturated acid when heated above its melting point and gives an *acetyl* derivative (XIII) when digested with acetic anhydride. It is somewhat remarkable that the acid yields neither a lactone nor an anhydride,



(XII.)



(XIII.)

since either the carboxyl groups or the hydroxyl and one carboxyl group must be in the *cis*-position. We are of opinion that the carboxyl groups are in the *trans*-position, because the acetyl derivative of the hydroxy-acid, when heated to its melting point, loses acetic acid and is converted quantitatively into an unsaturated acid, $C_{10}H_{14}O_4$, m. p. 257°. This acid is identical with the unsaturated acid (C) referred to on p. 78 and must be represented by formula (XIV) or (XV); there can be no doubt that it is 4 : 4 : 5-*trimethyl*-Δ^5-cyclo*pentene*-1 : 3-*dicarboxylic acid* (XIV). On oxidation with potassium permanganate, it yields a dibasic *keto-acid*, $C_9H_{14}O_5$, m. p. 125—126°, which, on further oxidation with sodium hypobromite, gives γ-methylbutane-$\alpha\beta\gamma$-tricarboxylic acid (XVIII). The keto-acid must therefore be *γ-acetyl-γ-methylbutane-$\alpha\beta$-di-*

carboxylic acid (XVII). γ-Methylbutane-$\alpha\beta\gamma$-tricarboxylic acid is also formed when 4 : 4 : 5-trimethyl-Δ^5-*cyclo*pentene-1 : 3-dicarboxylic acid is oxidised with dilute nitric acid.

(XIV.) $\begin{matrix} C(CO_2H)=\!=\!=C\cdot Me \\ CH_2\cdot CH(CO_2H)\cdot CMe_2 \end{matrix}$ $\qquad$ $\begin{matrix} C(CO_2H)-\!-\!-CHMe \\ CH\cdot CH(CO_2H)\cdot CMe_2 \end{matrix}$ (XV.)

(XVII.) $\begin{matrix} CO_2H \\ CH_2\cdot CH(CO_2H)\cdot CMe_2 \end{matrix}$ $\qquad$ $\begin{matrix} C\cdot OMe \\ C\cdot Me \end{matrix}$ $\qquad$ $\begin{matrix} CO_2H \\ CH_2\cdot CH(CO_2H)\cdot CMe_2 \end{matrix}$ $\qquad$ $\begin{matrix} CO_2H \\ CO_2H \end{matrix}$ (XVIII.)

When 4 : 4 : 5-trimethyl-Δ^5-*cyclo*pentene-1 : 3-dicarboxylic acid is oxidised with potassium permanganate at 0°, in addition to γ-acetyl-γ-methylbutane-$\alpha\beta$-dicarboxylic acid a second *keto-dicarboxylic acid*, $C_{10}H_{12}O_5$, m. p. 183—185°, is formed. This acid, which was characterised by the preparation of the *oxime* and *semicarbazone*, was unstable to potassium permanganate in alkaline solution. It was unfortunately not obtained in quantity and we are unable to suggest a satisfactory formula or account for its formation. The reaction would appear to be abnormal and recalls the conversion of Δ^1-*cyclo*hexeneacetic acid into 1-acetyl-Δ^1-*cyclo*pentene by an alkaline solution of potassium permanganate (Perkin and Wallach, *Ber.*, 1909, **42**, 145). On oxidation with dilute nitric acid, the keto-acid yielded γ-methylbutane-$\alpha\beta\gamma$-tricarboxylic acid, whilst on treatment with sodium hypobromite solution, although carbon tetrabromide and bromoform separated, the product was a resin which could not be crystallised and contained an appreciable quantity of bromine.

4 : 4 : 5-Trimethyl-Δ^5-*cyclo*pentene-1 : 3-dicarboxylic acid was somewhat resistant to reducing agents, but it was converted into the saturated *cyclo*pentane *acid* (XVI) by an excess of sodium and boiling amyl alcohol.

Unlike all the substances so far described, the unsaturated acid (D), m. p. 215—216° (p. 78) was optically active, the *sodium* salt being lævorotatory. Since the acid was racemised, with formation of the saturated cyclic acid (XVI), on reduction with sodium and amyl alcohol and yielded γ-methylbutane-$\alpha\beta\gamma$-tricarboxylic acid on oxidation with nitric acid, there can be no doubt that it is the lævo-form of (XIV).

(XVI.) $\begin{matrix} CH(CO_2H)-\!-\!-CHMe \\ CH_2\cdot CH(CO_2H)\cdot CMe_2 \end{matrix}$ $\qquad$ $\begin{matrix} C(:NOH)-CO-CHMe \\ CH_2\cdot CH(CO_2Me)\cdot CMe_2 \end{matrix}$ (XIX.)

The foregoing results appear to us to establish definitely that the keto-acid first described by Manasse and Samuel must be d-2 : 2 : 3-*trimethyl*cyclo*hexan*-4-*one*-1-*carboxylic acid* (II), and it became necessary once more to attempt the preparation of an oximino-derivative. Although neither the acid nor the methyl ester could be induced to react with benzaldehyde or piperonal, the methyl

ester reacted with amyl nitrite in the presence of sodium to yield an oil which was soluble in alkali and was evidently the crude *oximino-ester* (XIX). This ester could not be obtained crystalline, but on hydrolysis with formaldehyde and hydrochloric acid, followed by treatment with a dilute solution of potassium hydroxide, it gave an acid which partly crystallised on keeping. This acid, which was evidently somewhat impure 4-hydroxy-2 : 2 : 3-trimethyl-Δ^3-*cyclo*hexen-5-one-1-carboxylic acid (XI), was not purified, but was converted into the *cyclo*pentene acid by the reactions outlined above. The acid melted at 257° and was identical with that prepared from the dibromo-ester. The formation of 4 : 4 : 5-trimethyl-Δ^5-*cyclo*pentene-1 : 3-dicarboxylic acid in this manner would appear to eliminate definitely any possibility of molecular rearrangement during its formation from the bromo-ester.

The suggestion (*loc. cit.*, p. 1296) that the keto-acid can exist in keto- and enol forms has been confirmed by Mr. Aswath Narain Rao, who has prepared the *acetyl* derivative of the enolic form by treating camphorquinone with acetic anhydride and zinc chloride. This acetyl derivative is lævorotatory in chloroform solution and does not show mutarotation. It may be represented by formula (XX) or (XXI), and from analogy with the other unsaturated acids here referred to we are inclined to consider (XX) the more probable.

(XX.) $\begin{matrix} CH_2\text{—}C(OAc)\text{=}CMe \\ CH_2\cdot CH(CO_2H)\cdot CMe_2 \end{matrix}$ $\qquad$ $\begin{matrix} CH\text{=}C(OAc)\text{—}CHMe \\ CH_2\cdot CH(CO_2H)\cdot CMe_2 \end{matrix}$ (XXI.)

On hydrolysis, the acetyl derivative yields the ordinary ketonic form of the acid and all attempts to prepare it by direct acetylation have proved unsuccessful.

Since the acid previously considered to be *d*-2 : 2 : 4-trimethyl-*cyclo*hexan-3-one-1-carboxylic acid has now been shown to be *d*-2 : 2 : 3-trimethyl*cyclo*hexan-4-one-1-carboxylic acid, the constitution of some of the compounds prepared from it require revision. *trans-d*-3-Hydroxy-2 : 2 : 4-trimethyl*cyclo*hexane-1-carboxylic acid should be *trans-d*-4-hydroxy-2 : 2 : 3-trimethyl*cyclo*hexane-1-carboxylic acid (XXII), and the unsaturated acid derived therefrom must be represented by formula (XXIII) or (XXIV).

$\begin{matrix} CH_2\cdot CH(OH)\cdot CHMe \\ CH_2\text{—}CH\text{—}CMe_2 \\ \quad\quad CO_2H \end{matrix}$ (XXII.) $\qquad$ $\begin{matrix} CH\text{=}CH\text{—}CHMe \\ CH_2\cdot CH\cdot CMe_2 \\ \quad\quad CO_2H \end{matrix}$ (XXIII.) $\qquad$ $\begin{matrix} CH_2\cdot CH\text{:}CMe \\ CH_2\cdot CH\cdot CMe_2 \\ \quad\quad CO_2H \end{matrix}$ (XXIV.)

EXPERIMENTAL.

Bromination of Methyl 2 : 2 : 3-*Trimethyl*cyclo*hexan*-4-*one*-1-*carboxylate*. *Methyl* 5 : 5-*Dibromo*-2 : 2 : 3-*trimethyl*cyclo*hexan*-4-*one*-1-

carboxylate (VIII).—To a well-cooled solution of the crystalline methyl ester (55 g.) in acetic acid (280 c.c.), bromine (91·4 g.), dissolved in acetic acid (91·4 c.c.), was added. The reaction mixture was poured on to ice and the viscid oil which separated was washed with dilute aqueous sodium carbonate solution and dried in ethereal solution. On evaporation of the ether, the *dibromo-ester* was usually obtained as a brown oil, but in one experiment this gradually crystallised in needles; these were collected, drained on porous porcelain, and recrystallised from methyl alcohol, the dibromo-ester thus being obtained in glistening prisms, m. p. 57—58° (Found: Br, 45·1. $C_{11}H_{16}O_3Br_2$ requires Br, 44·9%).

Action of Barium Hydroxide on Methyl 5 : 5-*Dibromo*-2 : 2 : 3-*trimethyl*cyclo*hexan*-4-*one*-1-*carboxylate*.—A mixture of the crystalline (or liquid) dibromo-ester (26 g.) with a hot solution of barium hydroxide (52 g. in 170 c.c. of water) was boiled with constant agitation during 1 hour. The hot solution was filtered from a little insoluble matter (from which a further quantity of the mixed acids was obtained after treatment with a boiling solution of potassium hydroxide) and acidified. The liberated acids, which were isolated as a viscid brown oil (15 g.) by means of ether and partly crystallised on keeping, were esterified with methyl alcohol in the usual manner, and the esters formed were dissolved in ether. The ethereal solution was washed with dilute aqueous sodium carbonate (A), and then with 5% sodium hydroxide solution (B) until a test portion no longer gave a colour with ferric chloride. The ethereal solution was then dried and the solvent evaporated (C).

The sodium carbonate extract (A) on acidification yielded a small quantity of a resinous acid which was not further examined.

Methyl 4-*Hydroxy*-2 : 2 : 3-*trimethyl*-Δ^3-cyclo*hexen*-5-*one*-1-*carboxylate* (formula as XI).—The deep red sodium hydroxide extract (B) was saturated with carbon dioxide and the colourless crystalline solid that separated was collected (1·4 g.); the alkaline solution was then acidified and the viscid red oil produced was added to the mixture of acids obtained in later experiments and re-esterified.

The crystalline solid separated from light petroleum in rosettes of prismatic needles, m. p. 73—74° (Found: C, 61·9; H, 7·6. $C_{11}H_{16}O_4$ requires C, 62·3; H, 7·5%). The ester was appreciably soluble in hot water and dissolved readily in all the ordinary organic solvents except light petroleum, in which it was somewhat sparingly soluble. It gave with alcoholic ferric chloride a dirty green coloration, which was discharged by a trace of alkali.

The *dioxime*, which was obtained by heating the ester with hydroxylamine hydrochloride and sodium acetate in methyl-alcoholic solution, crystallised from benzene in fine needles, m. p.

138—139° (Found: C, 54·1; H, 7·5; N, 11·9. $C_{11}H_{18}O_4N_2$ requires C, 54·5; H, 7·4; N, 11·6%). In alcoholic solution it gave with ferric chloride a deep brown coloration. The *disemicarbazone* separated from hot water, in which it was somewhat readily soluble, in prisms, m. p. 206—207° (Found: N, 25·9. $C_{13}H_{22}O_4N_6$ requires N, 25·8%).

4-*Hydroxy*-2:2:3-*trimethyl*-Δ^3-cyclo*hexen*-5-*one*-1-*carboxylic acid* (XI), obtained by hydrolysing the methyl ester on the water-bath with a slight excess of dilute potassium hydroxide solution, crystallised from hot water or toluene in prismatic needles, m. p. 151—152° (Found: C, 60·8, 60·7; H, 7·4, 7·2. $C_{10}H_{14}O_4$ requires C, 60·6; H, 7·1%). It was readily soluble in hot water, alcohol, acetone, or ether, but more sparingly soluble in chloroform, benzene, or toluene, and gave a dirty bluish-green coloration with aqueous or alcoholic ferric chloride. In alkaline solution it immediately decolorised potassium permanganate, but it did not react with bromine. The acid was readily oxidised by hydrogen peroxide, but the crystalline products were too small in quantity for identification. It condensed with *o*-phenylenediamine, and on treatment with phenylhydrazine it gave a mixture of the *mono*- and the *di-phenylhydrazone* as a yellow, amorphous solid, which was purified by solution in alkali and precipitation by acid (Found: N, 11·5. $C_{16}H_{20}O_3N_2$ requires N, 9·7%. $C_{22}H_{26}O_2N_4$ requires N, 14·8%).

The *acetyl* derivative, prepared by digesting the acid with acetyl chloride, crystallised from water in irregular plates; these melted at 95° when air-dried and at 128° after being dried over sulphuric acid. They retained water of crystallisation (½ mol.) even after being kept for some months in a vacuum over phosphoric oxide (Found: C, 58·0; H, 6·7. $C_{12}H_{16}O_5,\frac{1}{2}H_2O$ requires C, 57·8; H, 6·8%).

Conversion of 4-*Hydroxy*-2 : 2 : 3-*trimethyl*-Δ^3-cyclo*hexen*-5-*one*-1-*carboxylic Acid into* 1-*Hydroxy*-4 : 4 : 5-*trimethyl*cyclo*pentane*-1 : 3-*dicarboxylic Acid* (XII).—A mixture of the hydroxyketo-acid (1 mol.) and 50% potassium hydroxide solution (3 mols.) was boiled for 1 hour. The product, obtained in quantitative yield on cooling and acidification, melted at 191—192° after crystallisation from hot water and was identified with the following acid by the mixed melting-point method (Found: C, 55·1; H, 7·9%).

1-*Hydroxy*-4 : 4 : 5-*trimethyl*cyclo*pentane*-1 : 3-*dicarboxylic Acid* (XII).—The ester fraction (C) (p. 82) distilled almost entirely at 150—160°/10 mm. as a colourless oil, which was a mixture. The ester from one experiment (55 g.) was heated with an excess of methyl-alcoholic potassium hydroxide on the water-bath for 1 hour, and the solution kept at 0° for 12 hours. A somewhat sparingly

soluble *potassium* salt separated in needles. This was well washed with ice-cold methyl alcohol (the filtrate, C_1, was reserved for later examination), dissolved in the minimum quantity of water, and acidified; a precipitate (16 g.) separated, and a little more was extracted from the filtrate with ether. 1-*Hydroxy*-4 : 4 : 5-*trimethyl*cyclo*pentane*-1 : 3-*dicarboxylic acid* thus obtained crystallised from hot water in glistening needles, m. p. 191—192° after softening at 184°, which contained $\frac{1}{2}H_2O$ (Found: C, 53·2; H, 7·8; H_2O, 4·0. $C_{10}H_{16}O_5,\frac{1}{2}H_2O$ requires C, 53·3; H, 7·6; H_2O, 4·0%. Found in material dried at 110°: C, 55·5; H, 7·5. $C_{10}H_{16}O_5$ requires C, 55·5; H, 7·4%). It was sparingly soluble in benzene, chloroform, or light petroleum, readily soluble in alcohol or acetic acid, gave no coloration with ferric chloride, was stable to potassium permanganate in alkaline solution, and was optically inactive.

The acid was treated with phosphorus pentachloride (3 mols.), and the product, after removal of the phosphorus oxychloride under diminished pressure, poured into formic acid. 4 : 4 : 5-Trimethyl-Δ^5-*cyclo*pentene-1 : 3-dicarboxylic acid, m. p. 257°, was thus obtained in poor yield; the other products of the reaction were not examined.

The *acetyl* derivative (XIII) formed when the hydroxy-acid was digested for 1 hour with an excess of acetic anhydride was obtained in needles on addition of water and concentration of the solution; it was recrystallised from hot water, in which it was somewhat sparingly soluble (Found: C, 55·7; H, 7·5. $C_{12}H_{18}O_6$ requires C, 55·8; H, 7·0%). It decomposed at 207—208° and immediately resolidified to a product, m. p. 257°, which was 4 : 4 : 5-trimethyl-Δ^5-*cyclo*pentene-1 : 3-dicarboxylic acid; the elimination of acetic acid is quantitative and this is the simplest method for the preparation of the pure unsaturated acid.

4 : 4 : 5-*Trimethyl*-Δ^5-cyclo*pentene*-1 : 3-*dicarboxylic Acid* (XIV).—The methyl-alcoholic solution (C_1, above) from which the potassium salt of the hydroxy-acid had been separated was freed from alcohol on the water-bath and acidified; the crystalline precipitate was collected (7 g.) and the filtrate (C_2) reserved. By recrystallising the former from methyl alcohol, 4 : 4 : 5-*trimethyl*-Δ^5-cyclo*pentene*-1 : 3-*dicarboxylic acid* was obtained in glistening rhombohedra, m. p. 257—258° (Found: C, 60·5; H, 7·2; *M*, 197·8. $C_{10}H_{14}O_4$ requires C, 60·6; H, 7·1%; *M*, 198). It was very sparingly soluble in water, ether, benzene, or chloroform, and more readily soluble in hot methyl alcohol, acetic acid, or formic acid. It immediately decolorised an alkaline solution of potassium permanganate, but reacted neither with bromine in acetic acid solution nor with sodium amalgam at the ordinary temperature. When heated above its

melting point, it did not yield an anhydride, but sublimed in long needles with very little decomposition. The aqueous solution of the *sodium* salt was optically inactive. The *dianilide*, prepared from the acid chloride in the usual manner, crystallised from dilute alcohol in fine needles, m. p. 200—201° (Found : C, 75·7 ; H, 7·4. $C_{22}H_{24}O_{22}N_2$ requires C, 75·9 ; H, 6·9%).

4 : 4 : 5-*Trimethyl*cyclo*pentane*-1 : 3-*dicarboxylic acid* (XVI) was obtained in an excellent yield when the unsaturated acid was reduced with sodium and amyl alcohol. It separated from hot water in soft, glistening prisms, m. p. 182—183°, and showed no tendency to yield an anhydride, small quantities distilling unchanged. It would appear, therefore, to be the *trans*-acid. It was readily soluble in hot water, alcohol, or ethyl acetate, and very sparingly soluble in benzene or chloroform (Found : C, 59·7 ; H, 8·3. $C_{10}H_{16}O_4$ requires C, 60·0 ; H, 8·0%).

1-4 : 4 : 5-*Trimethyl*-Δ^5-cyclo*pentene*-1 : 3-*dicarboxylic Acid*.—The filtrate (C_2), on extraction with ether, yielded a viscid yellow oil which could not be purified. Since it apparently contained a quantity of the hydroxy*cyclo*pentanedicarboxylic acid, it was digested with acetic anhydride and the crude acetyl derivative was heated at 200—210° until all evolution of acetic acid had ceased. The melt was dissolved in sodium carbonate solution, filtered from a little tar, and acidified. The solid which separated was collected, the filtrate (C_3) being reserved, and recrystallised from methyl alcohol, a further quantity of the *cyclo*pentene acid, m. p. 257°, being obtained. The methyl-alcoholic filtrate was evaporated, and the residue repeatedly crystallised from formic acid ; 1-4 : 4 : 5-*trimethyl*-Δ^5-cyclo*pentene*-1 : 3-*dicarboxylic acid* was thus obtained in irregular plates, m. p. 215—216° (Found : C, 60·5 ; H, 7·5. $C_{10}H_{14}O_4$ requires C, 60·6 ; H, 7·1%). This acid was very much more readily soluble in all the ordinary organic solvents than its inactive isomeride. On reduction with sodium and amyl alcohol, it yielded the inactive *cyclo*pentane acid (XVI). Under the conditions used for the oxidation of the racemic acid with nitric acid (see below), it gave γ-methylbutane-$\alpha\beta\gamma$-tricarboxylic acid, decomp. 154—155°, thus leaving no doubt as to its constitution. The sodium salt was lævorotatory in aqueous solution ; $[\alpha]_D^{25°}$ −62°.

The *dianilide* crystallised from dilute alcohol in glistening cubes, m. p. 208—209° (Found : N, 8·4. $C_{22}H_{24}O_2N_2$ requires N, 8·0%).

The filtrate (C_3, above) gave on extraction with ether a viscid oil which on trituration with formic acid yielded a further small quantity of the *l*-unsaturated acid. The formic acid mother-liquor contained an oil which was not examined.

Oxidation of 4 : 4 : 5-*Trimethyl*-Δ^5-cyclo*pentene*-1 : 3-*dicarboxylic Acid.*—(i) *With nitric acid.* The unsaturated acid (2 g.) was heated with nitric acid (*d* 1·2; 35 c.c.) on a water-bath for 8 hours and on a sand-bath for 8 hours; nitric acid (*d* 1·4; 15 c.c.) was then added, and the heating continued for a further 8 hours, a clear solution being obtained. The excess of mineral acid was removed on the water-bath; the viscid oily residue, on trituration with a little hydrochloric acid, crystallised almost completely. After draining on porous porcelain, it was recrystallised from a little hydrochloric acid, γ-methylbutane-$\alpha\beta\gamma$-tricarboxylic acid separating in rosettes of needles, decomp. 154—155° (Found: C, 47·2; H, 5·8; *M*, 205. Calc.: C, 47·1; H, 5·9%; *M*, 204). The identity of this acid was confirmed by the preparation of the anhydride, m. p. 142°.

(ii) *With potassium permanganate.* To a solution, at 0—5°, of the *cyclo*pentene acid (5 g.) in aqueous sodium carbonate through which a current of carbon dioxide was passing, 2·5% potassium permanganate solution (equiv. to 1 O_2) was added; the colour then remained permanent for 5 minutes. The filtered solution was concentrated in a current of carbon dioxide, acidified, and repeatedly extracted with ether and the extracts were dried and evaporated; a viscid brown oil remained which partly crystallised. This was triturated with concentrated hydrochloric acid, which removed a readily soluble brown oil (Z), and the residue was drained on porous porcelain and recrystallised from hydrochloric acid or from acetone–benzene; a *ketodicarboxylic acid* was thus obtained in glistening prisms, m. p. 182—183°, softening at 177° (Found: C, 56·4, 56·9; H, 6·0, 5·8; *M*, 212·6. $C_{10}H_{12}O_5$ requires C, 56·6; H, 5·6; *M*, 212). This acid was readily soluble in water, alcohol, ethyl acetate, or acetone, and more sparingly soluble in benzene or chloroform. It was slowly attacked by hot chromic acid solution, did not absorb bromine in acetic acid solution, and rapidly decolorised an alkaline solution of potassium permanganate at room temperature. It was readily oxidised by sodium hypobromite with formation of bromoform and carbon tetrabromide; the acid resulting from the oxidation was a gum which contained bromine and was not further examined. The salts of the keto-acid are readily soluble in water.

The *oxime* crystallised in small plates, decomp. 214°, containing apparently $\frac{1}{2}H_2O$ which it did not lose at 100° (Found: C, 50·6, 50·7; H, 5·8, 6·2. $C_{10}H_{13}O_5N,\frac{1}{2}H_2O$ requires C, 50·8; H, 5·9%). The *semicarbazone* crystallised from dilute alcohol in microscopic prisms, decomp. 241° (Found: C, 48·8; H, 5·9. $C_{11}H_{15}O_5N_3$ requires C, 49·1; H, 5·6%).

The keto-acid, on oxidation with nitric acid (*d* 1·2), gave an excellent yield of γ-methylbutane-$\alpha\beta\gamma$-tricarboxylic acid.

γ-Acetyl-γ-methylbutane-αβ-dicarboxylic Acid (XVII).—The hydrochloric acid solution (Z, above) gave, after the removal of the solvent in a vacuum over potassium hydroxide, a viscid brown oil. This (7 g.) was oxidised in sodium carbonate solution with potassium permanganate at 15—20°. Repeated extraction of the filtered, concentrated, and acidified solution with ether yielded an oil which partly crystallised. The solid was collected and recrystallised from dry ether, in which it was only sparingly soluble, *γ-acetyl-γ-methylbutane-αβ-dicarboxylic acid* separating in fine, glistening prisms, m. p. 125—126°. This acid was readily soluble in water or alcohol, but sparingly soluble in benzene or light petroleum. It did not react with phenylhydrazine or semicarbazide (Found: C, 53·1; H, 7·2. $C_9H_{14}O_5$ requires C, 53·5; H, 6·9%).

When a solution of the sodium salt of the keto-acid was treated with the calculated quantity of a solution of sodium hypobromite, bromoform immediately separated. After 1 hour, this was removed and the alkaline solution was acidified and extracted with ether; the oil obtained on removal of the solvent immediately crystallised and was identified as γ-methylbutane-αβγ-tricarboxylic acid.

Methyl 5-Oximino-2 : 2 : 3-trimethylcyclohexan-4-one-1-carboxylate (XIX).—Methyl *d*-2 : 2 : 3-trimethyl*cyclo*hexan-4-one-1-carboxylate (0·5 g.) was dissolved in ether containing finely divided sodium (0·06 g.), and to the well-cooled mixture *iso*amyl nitrite (0·26 g.) in ether was added. After the mixture had been kept at 0° for 12 hours the sodium had completely dissolved and a flocculent, yellow precipitate had separated. Ice was then added and the yellow, aqueous solution was separated and acidified. The brown oil obtained (0·3 g.), which showed no tendency to crystallise, was analysed after being kept for some days in a vacuum over sulphuric acid. The first and the second analysis refer to specimens prepared from the crystalline and the liquid ester, respectively (Found: N, 6·5, 6·7. $C_{11}H_{17}O_4N$ requires N, 6·2%). The *oximino-ester* was soluble in all the ordinary organic solvents and in a solution of potassium hydroxide, but was insoluble in aqueous sodium carbonate; it gave with alcoholic ferric chloride a deep brown coloration.

The ester * was hydrolysed by treatment with formaldehyde and hydrochloric acid, followed by dilute aqueous potassium hydroxide; the viscid oil obtained gave with ferric chloride a dirty bluish-green coloration. On keeping, the oil partly crystallised, but, as the quantity of material available was small, no attempt was made at purification and the oil was converted directly into 4 : 4 : 5-

* During the hydrolysis with potassium hydroxide amyl alcohol separated, indicating that "alcoholysis" with partial formation of the amyl ester had taken place during the reaction with amyl nitrite.

trimethyl-Δ^5-*cyclo*pentene-1 : 3-dicarboxylic acid by the methods already described. The *cyclo*pentene acid prepared in this manner crystallised from methyl alcohol in the characteristic rhombohedra, m. p. 257—258°, and was identical in every way with the acid prepared from the dibromo-ester.

1-4-*Acetyl*-2 : 2 : 3-*trimethyl*-Δ^3-cyclo*hexene*-1-*carboxylic Acid* (XX) [with ASWATH NARAIN RAO].—A mixture of camphorquinone (25 g.), acetic anhydride (75 c.c.), and freshly-fused zinc chloride (5 g.) was heated on a sand-bath, a vigorous reaction taking place with effervescence and evolution of heat. As soon as the reaction started, the source of heat was removed and the dark brown solution was allowed to cool, diluted with water (150 c.c.), and warmed on the water-bath for a short time to decompose the acetic anhydride. After 12 hours, the pale yellow precipitate of needles and tar was collected and washed with water (yield, 25·5 g.). The filtrate, on neutralisation of the excess of acetic acid with solid sodium carbonate, deposited a further quantity of solid (1 g.). The crude product was repeatedly extracted with dilute sodium carbonate solution until a test portion no longer gave a precipitate on acidification. The residue was extracted with dilute sodium hydroxide solution, which left undissolved camphorquinone (5·4 g.) and a little tar. The sodium hydroxide solution, on acidification, deposited a resinous mass which could not be purified. The deep brown sodium carbonate extract was carefully acidified with dilute sulphuric acid; after the addition of a small quantity of acid, the solution was extracted with ether to remove resinous impurities; on further addition of acid, an oil was deposited which, on evaporation of the dissolved ether, solidified. The crude acid (13·2 g.) was crystallised from hot water, dilute alcohol, or, preferably, light petroleum (b.p. 60—80°), 1-4-*acetyl*-2 : 2 : 3-*trimethyl*-Δ^3-cyclo*hexene*-1-*carboxylic acid* separating in colourless, transparent, glistening laminæ, m. p. 109—111° (Found: C, 63·2; H, 8·3; *M*, 224. $C_{12}H_{18}O_4$ requires C, 63·7; H, 8·0%; *M*, 226). In chloroform solution (1·283 g. in 25 c.c.), it showed $[\alpha]_D$ −66·3°, and this value did not alter during 48 hours. In carbon tetrachloride solution the acid absorbed an equivalent weight of bromine, hydrogen bromide being evolved, and on evaporation of the solvent a sharp-smelling oil remained. In alkaline solution, the acid was unstable to potassium permanganate; the products of the reaction could not be identified.

A solution of the acid (1 g.) in 15% sodium hydroxide solution (8 c.c.) was heated on the water-bath for 3 hours. On acidification of the cooled solution, an oil was precipitated which partly solidified over-night. The solid was separated, drained on porous porcelain, and recrystallised from water; it was then obtained in needles,

m. p. 69—70°. The anhydrous acid melted at 97—98°. It yielded a semicarbazone, m. p. 227—228°, and was identified as 2 : 2 : 3-trimethyl*cyclo*hexan-4-one-1-carboxylic acid by direct comparison with an authentic specimen. The oil extracted from the porous porcelain on which the keto-acid had been drained gave no colour with ferric chloride and evidently contained no hydroxy-acid. The enolic form, therefore, would appear to be incapable of existence. Attempts were made to acetylate the keto-acid directly, but in all cases the acid was recovered unchanged.

The authors wish to thank Dr. M. O. Forster, F.R.S., for much kindly criticism and also for permission to publish the experiments on *l*-4-acetyl-2 : 2 : 3-trimethyl-Δ^3-*cyclo*hexene-1-carboxylic acid, which were carried out under his direction.

INDIAN INSTITUTE OF SCIENCE,
BANGALORE. [*Received, October 11th*, 1926.]

XV.—*Substitution Products of 2-Aminodiphenyl.*

By HAROLD ARCHIBALD SCARBOROUGH and WILLIAM ALEXANDER WATERS.

THE orientation of substituents in 2-acetamido- and in 2-aminodiphenyl forms the second part of a series of investigations on the substitution products of the monoacid bases of the diphenyl series, of which the first part (J., 1926, 557) deals with the products of chlorination and bromination of 4-acetamido- and of 4-aminodiphenyl.

The only substitution product of 2-aminodiphenyl on record is a chlorinated base obtained by Hübner (*Annalen*, 1881, **209**, 339) on reduction of 2-nitrodiphenyl with tin and hydrochloric acid. The salts of this base were analysed, but no attempt was made to assign to it a definite structure. Later investigators, using less drastic methods for the reduction, have been unable to confirm the formation of such a base.

The scope of the present work was, first, a reinvestigation of the methods used in the reduction of 2-nitrodiphenyl, and, secondly, the preparation of the chloro-, bromo-, and nitro-derivatives of 2-acetamido- and of 2-amino-diphenyl.

On reduction of 2-nitrodiphenyl under normal conditions, substitution products of the base were not formed, but on reduction with tin and hydrochloric acid under conditions favourable to indirect chlorination (compare Blanksma, *Rec. trav. chim.*, 1906, **25**,

365) a mixture of approximately 60% of 5-chloro-2-aminodiphenyl and 40% of 2-aminodiphenyl was produced.

Direct chlorination of 2-aminodiphenyl in carbon tetrachloride solution proceeded smoothly and gave a quantitative yield of 3 : 5-dichloro-2-aminodiphenyl hydrochloride. Direct chlorination of the acetylated base invariably yielded gummy products, from which were isolated mixtures of 5-chloro-2-acetamidodiphenyl and unchanged 2-acetamidodiphenyl; and a prolonged action of chlorine yielded a tar from which a pure substance could not be isolated.

2-Acetamidodiphenyl yielded a stable *N*-chloroamine, which could be converted, on treatment with alcohol and acetic acid, into a mixture of 5-chloro-2-acetamidodiphenyl and 2-acetamidodiphenyl. This partly chlorinated mixture could not be separated into its components on account of the very slight differences in solubility of the two substances in all the usual organic solvents. By treating the mixture with sodium hypochlorite, a *N*-chloroamine was formed by both substances, and on conversion with acetic acid in alcohol pure 5-chloro-2-acetamidodiphenyl was obtained. Free chlorine was observed during the conversion, and this fact may be taken as an indication that *N* : 5-dichloro-2-acetamidodiphenyl cannot be transformed into a dichloro-derivative substituted in either ring. This behaviour is the same as that of *N* : 3-dichloro-4-acetamidodiphenyl (*loc. cit.*).

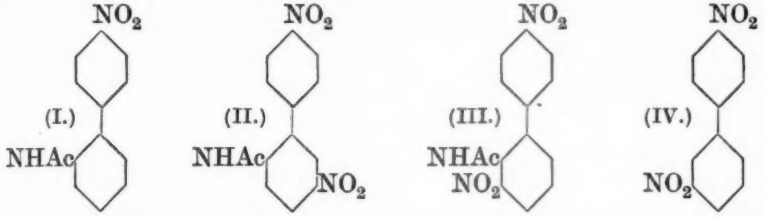
Bromination of the free base in carbon tetrachloride solution yielded 5-bromo-2-aminodiphenyl hydrobromide; bromination in acetic acid solution resulted in a quantitative yield of 3 : 5-dibromo-2-aminodiphenyl, provided that care was taken to remove from the reaction mixture the hydrogen bromide formed. Direct bromination of the base under various conditions did not give a more highly brominated product which could be isolated.

2-Acetamidodiphenyl yielded an impure *N*-bromo-derivative which could not be purified by crystallisation from non-hydroxylic solvents. The impure product on treatment with acetic acid was transformed partly into 5-bromo-2-acetamidodiphenyl and partly into 2-acetamidodiphenyl with the liberation of free bromine.

Direct bromination of the acetyl derivative in acetic acid solution at room temperature yielded 5-bromo-2-acetamidodiphenyl; more highly brominated products were obtained in very small yields only on prolonged exposure to sunlight. On bromination at 100°, 3 : 5-dibromo-2-aminodiphenyl was obtained either by the further bromination of the monobromoacetyl derivative and subsequent hydrolysis, or by bromination of 5-bromo-2-aminodiphenyl after hydrolysis had taken place.

On nitration of 2-acetamidodiphenyl in a mixture of acetic acid

and sulphuric acid at 0°, an approximately 50% yield of 4′-nitro-2-acetamidodiphenyl (I) was obtained; the residue was a yellow gum from which a crystalline product could not be isolated. By the further nitration of 4′-nitro-2-acetamidodiphenyl, or of the residual gum, a dinitro-2-acetamidodiphenyl was obtained. This product on hydrolysis and deamination yielded 3 : 4′-dinitrodiphenyl (IV), and must therefore have the constitution of a 5 : 4′-dinitro- (II) or of a 3 : 4′-dinitro-2-acetamidodiphenyl (III).



A conclusive proof of the structure of this dinitro-compound could not be obtained owing to the symmetry of the molecule, but if consideration is given to the chlorination and bromination products of 2-acetamidodiphenyl, it would appear that the most probable structure is 5 : 4′-dinitro-2-acetamidodiphenyl (II).

The structures of the substitution products of 2-aminodiphenyl and of its acetyl derivative are in agreement with those to be expected from an application of the tentative rules for substitution in the diphenyl series which were suggested in the previous communication (*loc. cit.*).

Although it may be seen that the amino-group and groups derived therefrom tend to promote substitution in the same nucleus, yet the nitration of 2-acetamidodiphenyl to yield a product substituted in the 4′-position gives a second instance of substitution in the opposite nucleus when conditions for indirect substitution are not favourable.

This anomalous effect can hardly be ascribed to steric influences, since the para-position to the acetamido-group is available, and this position is not adjacent to any large hindering group as was the case in the bromination of 4-acetamidodiphenyl.

EXPERIMENTAL.

2-Aminodiphenyl.—(*a*) 25 G. of 2-nitrodiphenyl (van Hove, *Bull. Acad. Roy. Belg.*, 1922, **8**, 505) were added to a solution of 105 g. of stannous chloride in 500 c.c. of ether obtained by passing in dry hydrogen chloride. After 24 hours, the ether was removed and the base was liberated with sodium hydroxide and distilled in a vacuum (compare Dimroth, *Ber.*, 1907, **40**, 2378).

(*b*) 37 G. of 2-nitrodiphenyl, dissolved in 300 c.c. of alcohol, were

added slowly to a solution of 240 g. of stannous chloride in 240 c.c. of concentrated hydrochloric acid. The alcohol was removed after refluxing for 3 hours, and the base liberated and purified as described above.

2-Aminodiphenyl was thus obtained as a white solid, b. p. 170°/15 mm., m. p. 49—50°. Previously recorded values of the m. p. vary between 44° and 49°.

2-*Acetamidodiphenyl* was prepared by adding 1·5 mols. of acetyl chloride drop by drop to a solution of the base in dry pyridine (5 parts) at 0°. After 20 minutes, the mixture was poured into an excess of ice-cold dilute hydrochloric acid. The substance crystallised from dilute alcohol or light petroleum (b. p. 60—80°) in white needles, m. p. 121° (corr.). Previously recorded values of the m. p. vary between 117·5° and 119°. Acetylation of the base by heating with acetic acid or a mixture of acetic acid and acetic anhydride was unsatisfactory, the oily product crystallising only with difficulty and with considerable loss. Samples of 2-aminodiphenyl contaminated with a little 4-aminodiphenyl were acetylated, and the mixed acetyl derivatives treated, in a Soxhlet apparatus, with light petroleum (b. p. 40—60°), in which the 4-acetamidodiphenyl is insoluble.

Chlorination on Reduction of 2-Nitrodiphenyl.—A solution of 10 g. of 2-nitrodiphenyl in 100 c.c. of alcohol and 200 c.c. of concentrated hydrochloric acid was boiled under reflux, and granulated tin (10 g.) was added, each piece after the preceding one had dissolved. The alcohol was distilled off and the bases were liberated with sodium hydroxide. The product, isolated and dried in ether, distilled at 170—190°/15 mm. and partly solidified on cooling (Found: Cl, 10·4%, which corresponds with 60% of a monochloro-base). The mixed bases were benzoylated and 5-chloro-2-benzamidodiphenyl, m. p. 142°, was isolated by fractional crystallisation.

3 : 5-*Dichloro-2-aminodiphenyl.*—A slight excess of a saturated solution of chlorine in carbon tetrachloride was added to an ice-cold 5% solution of 2-aminodiphenyl in the same solvent. The white precipitate which separated was collected after an hour, washed with carbon tetrachloride, and dried in the air; 3 : 5-*dichloro-2-aminodiphenyl hydrochloride* was then obtained, m. p. 140—145° (decomp.) (Found: HCl, 13·4. $C_{12}H_9NCl_2,HCl$ requires HCl, 13·3%). Warming with dilute ammonia gave 3 : 5-*dichloro-2-aminodiphenyl*, which crystallised from dilute alcohol in white needles, m. p. 51° (Found: Cl, 29·6. $C_{12}H_9NCl_2$ requires Cl, 29·8%). On benzoylation (Schotten–Baumann) 3 : 5-*dichloro-2-benzamidodiphenyl* was obtained, which crystallised from alcohol in long needles, m. p. 207° (Found: Cl, 20·7. $C_{19}H_{13}ONCl_2$ requires Cl, 20·7%).

Chlorination in acetic acid solution yielded tar-like products from which crystalline compounds could not be obtained.

3 : 5-*Dichlorodiphenyl*, obtained from 3 : 5-dichloro-2-aminodiphenyl hydrochloride by the elimination of the amino-group in the usual manner, was a pale yellow oil, b. p. 180°/15 mm. On oxidation with chromic anhydride in glacial acetic acid solution, it yielded 3 : 5-dichlorobenzoic acid, m. p. 188°.

N-*Chloro*-2-*acetamidodiphenyl*.—To a suspension of 10·6 g. of 2-acetamidodiphenyl in a solution of 20 g. of sodium bicarbonate in 200 c.c. of water, 150 c.c. of *N*-sodium hypochlorite were added during 2 hours. The precipitate was collected after 12 hours, washed with cold water, dried, and fractionally crystallised from light petroleum (b. p. 40—60°), the more soluble fraction being preserved. The *chloroamine* was thus obtained in colourless needles, m. p. 86° (Found : available Cl, 13·9. $C_{14}H_{12}ONCl$ requires Cl, 14·4%).

Conversion of the N-*Chloroamine*.—A mixture of 5 g. of the chloroamine, 100 c.c. of alcohol, and 5 c.c. of glacial acetic acid was warmed gently until it gave no reaction with potassium iodide. Water was then added to start precipitation, and the solid matter which separated on cooling was crystallised fractionally from light petroleum (b. p. 60—80°), and also from dilute aqueous solutions of alcohol, acetone, and acetic acid. The product formed white crystals which melted over the range 110—120° according to the specimen, but it was not possible to separate the constituents : m. p. after two crystallisations, 116° (Found : Cl, 11·6%); m. p. after six crystallisations, 120° (Found : Cl, 12·2%); m. p. of another preparation, 118° (Found : Cl, 10·4%). $C_{14}H_{12}ONCl$ requires Cl, 14·4%.

By treatment of the mixture with sodium hypochlorite, followed by conversion with dilute acetic acid as previously described, chlorine was evolved and pure 5-*chloro*-2-*acetamidodiphenyl* was obtained, which crystallised from dilute alcohol or light petroleum in long needles, m. p. 122·5° (Found : Cl, 14·6. $C_{14}H_{12}ONCl$ requires Cl, 14·4%). From this substance, 5-*chloro*-2-*benzamidodiphenyl* was obtained, which crystallised from dilute alcohol in colourless needles, m. p. 142—143° (Found : Cl, 11·6. $C_{19}H_{14}ONCl$ requires Cl, 11·5%).

The yield of crystalline solids in both *N*-chloroamine transformations was small, as the residues from the crystallisation were dark oils from which pure substances could not be separated.

Direct Chlorination of 2-*Acetamidodiphenyl*.—A 2% solution of 2-acetamidodiphenyl in glacial acetic acid, containing a large excess of anhydrous sodium acetate, was cooled in water and a mixture of

chlorine and carbon dioxide was passed in slowly until the gain in weight corresponded to the formation of a monochlorinated compound; the mixture was then poured on to ice and water. A yellow gum separated which became semi-solid and crystallised from light petroleum as a white powder consisting of 5-chloro-2-acetamidodiphenyl and 2-acetamidodiphenyl. A similar mixture was obtained by chlorination in carbon tetrachloride solution. A solid could not be separated if the chlorination was carried on to a higher stage of substitution.

2 : 5-*Dichlorodiphenyl*.—5 G. of 5-chloro-2-acetamidodiphenyl were hydrolysed by boiling for a day with 10% alcoholic hydrochloric acid. The hydrochloride of the base, which separated after the removal of the alcohol, was converted into the corresponding dichlorodiphenyl by the Sandmeyer reaction. A light yellow oil (2 g.) was obtained, b. p. 171°/15 mm. (Found : Cl, 31·25. $C_{12}H_8Cl_2$ requires Cl, 31·8%). This crude product was oxidised by chromic anhydride in glacial acetic acid solution to 2 : 5-dichlorobenzoic acid, m. p. 154°.

N-*Bromo*-2-*acetamidodiphenyl* was prepared in a similar manner to the corresponding chloro-compound. It was a pale yellow powder, easily soluble in non-hydroxylic solvents, and could not be obtained of a greater purity than about 70%. On treatment with alcohol and acetic acid, it decomposed with the liberation of bromine, and yielded a mixture of 5-bromo-2-acetamidodiphenyl, m. p. 130°, and 2-acetamidodiphenyl.

5-*Bromo*-2-*acetamidodiphenyl*.—A cold 10% solution of 2-acetamidodiphenyl in glacial acetic acid was treated with bromine (1 mol.) as a 10% solution in the same solvent. After 1 day, the mixture was poured into water; the brominated compound, which was precipitated in an almost quantitative yield, crystallised from dilute alcohol in white needles, m. p. 130° (Found : Br, 27·7. $C_{14}H_{12}ONBr$ requires Br, 27·6%).

By the hydrolysis of this acetyl derivative with 10% alcoholic hydrobromic acid 5-*bromo*-2-*aminodiphenyl* was obtained. It crystallised from dilute alcohol in white needles, m. p. 57·5° (Found : Br, 32·0; C, 58·1; H, 4·15. $C_{12}H_{10}NBr$ requires Br, 32·1; C, 58·1; H, 4·0%). This base on benzoylation (Schotten–Baumann) gave 5-*bromo*-2-*benzamidodiphenyl*, which crystallised from alcohol in white needles, m. p. 162° (Found : Br, 22·9. $C_{19}H_{14}ONBr$ requires Br, 22·7%).

2 : 5-*Dibromodiphenyl*, obtained from 5-bromo-2-aminodiphenyl by the Sandmeyer reaction, was a yellow oil, b. p. 209°/15 mm., which became very viscous but did not solidify on cooling to 0° (Found : Br, 51·4. $C_{12}H_8Br_2$ requires Br, 51·3%). On oxidation

with chromic anhydride in glacial acetic acid solution it yielded 2 : 5-dibromobenzoic acid, m. p. 156°.

5-Bromo-2-aminodiphenyl Hydrobromide.—A 10% solution of 2-aminodiphenyl in carbon tetrachloride was treated with slightly more than one molecular equivalent of bromine as a 5% solution in the same solvent. The light yellow precipitate which formed was filtered off after an hour, washed with carbon tetrachloride, and dried in the air. It had a m. p. of 226°, but it could not be crystallised on account of the ease with which it was hydrolysed (Found : HBr, 24·4. $C_{12}H_{10}NBr,HBr$ requires HBr, 24·6%). On treatment with ammonia, it yielded the corresponding base as a viscous oil. This, on benzoylation, gave 5-bromo-2-benzamidodiphenyl, which alone or mixed with a specimen prepared by the alternative method melted at 161—162°.

3 : 5-*Dibromo-2-aminodiphenyl.*—To 5 g. of 2-aminodiphenyl, dissolved in 50 c.c. of glacial acetic acid, 5 g. of powdered anhydrous sodium acetate were added and the mixture was cooled in ice-water while 100 c.c. of a 10% solution of bromine in glacial acetic acid were run in slowly until the bromine was no longer decolorised. The mixture was poured on to ice and water. The brown oil thrown down soon solidified and crystallised from dilute alcohol in needles, m. p. 51—52° (Found : Br, 48·8. $C_{12}H_9NBr_2$ requires Br, 48·9%). The yield is quantitative, but if no sodium acetate be added to remove the hydrogen bromide produced by the reaction only viscous black oils can be obtained.

The *benzoyl* derivative crystallised from alcohol in white needles, m. p. 218° (Found : Br, 37·0. $C_{19}H_{13}ONBr_2$ requires Br, 37·1%). On eliminating the amino-group from the base in the usual manner 3 : 5-*dibromodiphenyl*, b. p. 208°/15 mm., was obtained (compare J., 1926, 561). It was oxidised to 3 : 5-dibromobenzoic acid, m. p. 212°.

Further Bromination of 5-Bromo-2-acetamidodiphenyl.—Only small traces of more highly brominated products could be obtained by exposing a solution of 5-bromo-2-acetamidodiphenyl and bromine, containing a little iodine as a catalyst, to sunlight for more than a week. On heating the mixture to 100°, bromination occurred together with hydrolysis of the acetyl derivative, for, on pouring the product into water, a dark oil separated which, on benzoylation, yielded 3 : 5-dibromo-2-benzamidodiphenyl; this melted at 218°, alone or mixed with a sample prepared by the alternative method.

Nitration of 2-Acetamidodiphenyl.—15 G. of 2-acetamidodiphenyl, dissolved in 15 c. c. of glacial acetic acid and 30 c.c. of concentrated sulphuric acid at 0°, were slowly treated with a mixture of 6 c.c. of fuming nitric acid and 14 c.c. of glacial acetic acid. After an hour, the product was poured on to ice; the yellow solid was filtered off,

washed with dilute sodium carbonate solution, and fractionally crystallised from alcohol; 8 g. of pale yellow needles, m. p. 199°, were thus obtained, consisting of *4′-nitro-2-acetamidodiphenyl* (Found: N, 10·8. $C_{14}H_{12}O_3N_2$ requires N, 10·9%). The residual alcoholic solutions, on evaporation, yielded a reddish-yellow gum from which it was not possible to isolate any other substitution product.

By the hydrolysis of the acetyl derivative with 10% alcoholic hydrochloric acid, *4′-nitro-2-aminodiphenyl* was obtained. It crystallised from alcohol in orange-red needles, m. p. 158° (Found: N, 13·3. $C_{12}H_{10}O_2N_2$ requires N, 13·1%).

4′-Nitro-2-bromodiphenyl, obtained from the base by the Sandmeyer reaction, crystallised from alcohol in bright yellow needles, m. p. 82·5° (Found: Br, 28·5. $C_{12}H_8O_2NBr$ requires Br, 28·7%). On oxidation with chromic anhydride in glacial acetic acid solution, bromine was evolved and *p*-nitrobenzoic acid was produced, m. p. 240—241°.

Dinitration of 2-Acetamidodiphenyl.—The nitration was carried out under conditions similar to those given above, but with the use of a double quantity of nitric acid, and the mixture was kept for 24 hours before the products were separated. The solid product was extracted with alcohol, and the insoluble residue was crystallised from benzene; it then formed pale yellow prisms, m. p. 211°, of 5(or 3) : 4′-*dinitro-2-acetamidodiphenyl* (Found: N, 14·1. $C_{14}H_{11}O_5N_3$ requires N, 14·0%). This substance yielded *p*-nitrobenzoic acid (m. p. 240—241°) on oxidation with chromic and glacial acetic acids, showing that one of the nitro-groups was in the 4′-position.

The same dinitro-compound could be isolated by further nitration of the gum produced in the less drastic nitration reaction, but in no case was the total yield more than 60%. The residue consisted of the usual, more soluble, oily products. On hydrolysis with alcoholic hydrochloric acid, the *base* corresponding to the acetyl derivative was obtained. It separated from alcohol as a bright yellow powder, m. p. 238° (Found: N, 16·35. $C_{12}H_9O_4N_3$ requires N, 16·2%).

By eliminating the amino-group from this compound by the usual method, 3 : 4′-*dinitrodiphenyl* was obtained; it melted at 189°, alone or mixed with a specimen obtained by the elimination of the amino-group from 3 : 4′-dinitro-4-aminodiphenyl.

All the m. p.'s recorded in this paper have been corrected, and where necessary the identity of a substituted benzoic acid has been established by the "mixed m. p." method.

The authors beg to thank the Chemical Society for a grant from the Research Fund. One of the authors (W. A. W.) desires to thank

the Master and Fellows of Gonville and Caius College for a studentship, and the Advisory Council of the Department of Scientific and Industrial Research for a grant, which have enabled him to collaborate in this work.

THE UNIVERSITY CHEMICAL LABORATORIES,
CAMBRIDGE. [*Received, November 13th*, 1926.]

XVI.—*The Vapour Pressures of Mixtures of* (a) *Methyl Acetate and Water;* (b) *Methyl Acetate, Sucrose, and Water.*

By ANDREW MCKEOWN and FLAXNEY PERCIVAL STOWELL.

THE measurements now recorded were carried out with the primary object of testing various "activity" theories of reaction velocity in the special case of the hydrolysis of methyl acetate by acids. Whilst no satisfactory conclusions could be drawn from their application in this connexion, the data may be of value from the point of view of thermodynamic theory, or they may be of use to other workers in the field of chemical kinetics.

The activities of the two volatile constituents in ester–water and ester–sucrose–water mixtures have been obtained by measurement of their partial vapour pressures, which represent the respective activities with sufficient accuracy for most purposes. As a check, the total vapour pressure of each system investigated has also been determined by an independent method. In the case of ester–water mixtures, concentrations of ester up to about 2*N* have been used. All the ester–sucrose–water mixtures contained a constant small concentration of ester, the sucrose content varying up to 600 g. per litre of solution. This involves a considerable variation in the concentration of water. All measurements have been carried out at two temperatures, *viz.*, 25° and 35°.

EXPERIMENTAL.

Total Vapour Pressures.—The static method of measurement adopted was very similar to that proposed by Morton (*J. Soc. Chem. Ind.*, 1919, **38**, 363T). A few practical modifications may be mentioned. In place of the jacketing arrangement indicated in Morton's diagram, the two barometer tubes and the capillary tubes attached to their upper ends pass through the bottom of a thermostat maintained at the working temperature. The lower ends of the barometer tubes dip below the surface of mercury in a closed container. This arrangement avoids the necessity for rubber joints

and connexions and consequent fouling of the mercury. A small sealed glass stirrer containing a bundle of soft-iron rods is placed in the barometer tube which contains the experimental mixture. This stirrer, operated from outside by an electromagnet, facilitates the removal from the liquid of dissolved air, which is then pumped out through the capillary. Before the hydrostatic levels of mercury and solution in the tubes are read, the stirrer is lifted out of the solution and suspended above its surface by means of the electromagnet. The levels are read off through a telescope on an accurately graduated glass scale placed behind the tubes. In order to dispense with the precautions necessary to ensure a complete vacuum in the comparison tube (a trace of moisture in this would, of course, lead to erroneous results), it has been found convenient to retain a few c.c. of air-free water over the mercury surface in this tube. The vapour pressure of the mixture under examination is then compared, not against zero pressure, but against the pressure of saturated aqueous vapour at the same temperature. A glass tap at the end of the capillary tube attached to the comparison tube prevents the expulsion of this water at each pumping operation which is carried out for the other tube.

For the purpose of vapour-pressure measurements, the purest methyl acetate is essential. Kahlbaum's ester was therefore purified by the method recommended by Young and Thomas (J., 1893, **63**, 1191). The pure product distilled between 56·9° and 57·1° (standardised thermometer) at 760 mm. (Young and Thomas give 57·1°.) The vapour pressure of the pure ester was 214·9 mm. at 25° and 328·6 mm. at 35°, as compared with 215·0 and 327·5 mm., respectively, interpolated from Young and Thomas's data. The ester had $d_4^{15°}$ 0·9355 (compare 0·9359, given by the same authors).

Table I gives the total vapour pressures of various ester–water mixtures at 25° and 35°. The normalities refer to 15°, and the pressures are expressed in mm. Hg at 0°. Each figure represents the mean of a number of determinations with different samples of duplicate stock solutions. The variation from this mean was usually of the order $\pm 0{\cdot}2\%$, and this probably represents the maximum error in the data. Table II contains the total vapour pressures of ester–sucrose–water mixtures, each of which was $0{\cdot}2542N$ with respect to ester. With increasing sucrose content, duplication became less satisfactory, probably owing to increasing difficulty in getting rid of dissolved air as the solutions became more viscous, and the possible error in the data for the highest concentrations of sucrose is about $\pm 0{\cdot}5\%$.

From Table II it is seen that the total vapour pressure of a solution which is $0{\cdot}2542N$ with respect to ester rises rapidly as the sucrose

TABLE I.

Total Vapour Pressures of Ester–Water Mixtures at 25° and 35°.

Mols. of ester per litre of soln.	Mols. of water per litre of soln.	Total vapour pressure at 25°.	Total vapour pressure at 35°.
0	55·4	23·8	42·2
0·2542	54·5	46·0	80·2
0·5084	53·6	67·2	115·9
1·017	51·6	108·2	176·8
1·525	49·4	144·2	225·1
2·033	47·3	172·2	265·4
Pure ester.	—	214·9	328·6

TABLE II.

Total Vapour Pressures of Ester–Sucrose–Water Mixtures at 25° and 35°.

(Constant concentration of ester = 0·2542 mol./litre.)

G. of sucrose per litre of soln.	Mols. of water per litre of soln.	Total vapour pressure at 25°.	Total vapour pressure at 35°.
0	54·5	46·0	80·2
100	51·0	48·2	83·2
200	47·6	51·4	87·3
300	44·1	55·6	92·8
400	40·7	60·5	99·5
500	37·2	66·7	108·0
600	33·6	75·5	120·8

content increases. This effect is not unexpected in view of the marked displacing effect of the sucrose in solution. This produces a very appreciable increase in the molar fraction of the more volatile component—the ester—with increasing concentration of sucrose.

Partial Vapour Pressures.—These have been determined by the well-known dynamical method. This involves the saturation of a known volume of an indifferent gas with the vapours in equilibrium with the liquid mixture under examination and analysis of the resulting gaseous mixture. In the present work, estimation by a direct absorption method of the amount of each component carried over as vapour is rendered impossible by the fact that the ester vapour would react with any of the reagents normally used for the removal of water vapour. An indirect method of analysis, depending on the combustion of the mixed vapours and subsequent estimation of the products of combustion, was therefore adopted. The same method has been employed by Linebarger (*J. Amer. Chem. Soc.*, 1895, **17**, 615), by Foote and Scholes (*ibid.*, 1911, **33**, 1309), and by Wright (J., 1922, **121**, 2251). The data obtained by Foote and Scholes for the partial vapour pressures of ethyl alcohol and water over alcohol–water mixtures indicate that, with suitable

precautions, a fair degree of accuracy can be obtained by this mode of analysis.

Details of the experimental method need not be given. The main features of the technique involve an accurate knowledge of the volume, temperature, and pressure of the air which is to be saturated, and of the pressure of the gas mixture when it leaves the last saturator; the use of an efficient train of saturators; the introduction of an auxiliary oxygen supply beyond the last of these; prevention of condensation of the vapours from the saturated air current; and the usual precautions incidental to combustions.

The partial vapour pressures p_e and p_w of ester and water respectively are given by the relations:

$$p_e = xR\theta(P + p_m - p_s)/132PV,$$
$$p_w = (y - 0{\cdot}4095x)R\theta(P + p_m - p_s)/18PV,$$

where x and y are the weights of carbon dioxide and water resulting from saturation of V litres of dry air measured under atmospheric pressure, P, and at the working temperature $\theta°$ Abs., p_m is the working pressure in excess of atmospheric as registered on an auxiliary manometer beyond the last saturator, p_s is the total vapour pressure of the solution, and R is the gas constant expressed in litre-millimetres. In the above equations, the value of p_s already obtained by the static method may be employed, or, alternatively, we need not assume that p_s is known, but substitute $p_s = p_e + p_w$, and solve the two simultaneous equations for p_e and p_w. These methods of calculation lead to substantially the same values of p_e and p_w.

Any experimental error usually affects the value obtained for the partial pressure of water much more than that of ester. The value of p_w is determined by difference between the total water found and the water corresponding to combustion of the ester vapour, and the latter quantity is usually several times greater than the weight of water corresponding to p_w. Hence any error in the estimation of the carbon dioxide (which determines the value of p_e) produces a much greater error in the value of p_w. In the case of the highest concentrations of ester used, an error of 1 mg. in the weight of the carbon dioxide would only affect the value of p_e by 0·1%, but would introduce a 4% error into p_w. The partial pressure of the water might, of course, be obtained indirectly by subtraction of the observed partial pressure of ester from the total vapour pressure of the solution independently obtained.

Tables III and IV contain the results for ester–water and ester–sucrose–water mixtures, respectively, at 25° and 35°. In cols. 2 and 3 of the tables the sum of the observed partial pressures p_e and

p_w is compared with the total vapour pressure p_s obtained by the static method.

TABLE III.

Partial Vapour Pressures of Ester and Water over Ester–Water Mixtures.

Conc. of ester.	p_s.	$p_e + p_w$ (obs.).	p_e. (obs.).	p_e (calc.).	p_w (obs.).	p_w (calc.).
At 25°.						
0·2542	46·0	46·5	22·5	22·3	24·0	23·7
0·5084	67·2	67·8	43·7	43·7	24·1	23·5
1·017	108·2	108·8	85·3	84·9	23·5	23 3
1·525	144·2	144·8	122·0	121·1	22·8	23·1
2·033	172·2	172·5	149·2	149·4	23·3	22·8
At 35°.						
0·2542	80·2	80·4	38·3	38·2	42·1	42·0
0·5084	115·9	115·8	73·9	74·1	41·9	41·8
1·017	176·8	176·4	134·8	135·4	41·6	41·4
1·525	225·1	224·5	183·9	184·2	40·6	40·9
2·033	265·4	267·5	226·6	224·9	40·9	40·5

TABLE IV.

Partial Vapour Pressures of Ester and Water over Ester–Sucrose–Water Mixtures.

(Constant concentration of ester = 0·2542N.)

G. of sucrose per litre of soln.	p_s.	$p_e + p_w$. (obs.).	p_e. (obs.).	p_e. (calc.).	p_w. (obs.).	p_w. (calc.).
At 25°.						
0	46·0	46·5	22·5	22·3	24·0	23·7
100	48·2	48·1	24·6	24·7	23·5	23·5
200	51·4	51·4	28·1	28·1	23·3	23·3
300	55·6	55·5	32·3	32·5	23·2	23·1
At 35°.						
0	80·2	80·4	38·3	38·2	42·1	42·0
100	83·2	82·8	41·3	41·5	41·5	41·7
200	87·3	87·4	45·6	45·9	41·8	41·4
300	92·8	92·2	51·5	51·7	40·7	41·1
400	99·5	99·4	58·6	58·9	40·8	40·6

Discussion of Results.

The values given under p_e (calc.) and p_w (calc.) in Table III are derived as follows. The highest concentration of ester employed is 2·033N, and represents a molar fraction of ester of 0·04117. All the mixtures used are therefore relatively dilute solutions of ester in water and should conform more or less to Raoult's law, *i.e.*, the partial pressure of the solvent water should be approximately equal to the vapour pressure of pure water multiplied by the molar fraction of water in the solution. This gives p_w (calc.), and, subtracting this from the total vapour pressure p_s, the value of p_e (calc.) is obtained.

The general agreement between the observed and the calculated partial pressures in Table III indicates that Raoult's law is valid as a rough approximation for the solvent. It cannot, however, be strictly applicable over the whole range studied, since Henry's law is not obeyed by the solute. The curve obtained by plotting p_e against the molar fraction of ester (N_e) is uniformly concave to the N_e-axis. If we make the probable assumption that very dilute solutions of ester in water obey Raoult's law, it can readily be shown that over the same range of concentration the plot of p_w against N_e is convex to the N_e-axis. This implies that p_w (obs.) should always be greater than p_w (calc.), and that the divergence should be greater the greater the concentration of ester. Our experimental data for p_w (obs.), however, are not sufficiently accurate to afford a test of this point.

Considerable difficulty was experienced in obtaining trustworthy results for ester–sucrose–water mixtures. For solutions of high sucrose content the results were altogether untrustworthy, the partial pressure of ester being abnormally small and that of the water abnormally great. This is just what would be expected if the air current were incompletely saturated with the mixed vapours, and it is probable that the train of saturators used was not efficient enough for the more viscous sucrose solutions. Such data as appear to be trustworthy are in Table IV. As in the case of the ester-water mixtures, the experimental values of the partial pressures are compared with the figures calculated on the assumption that the component water obeys Raoult's law. In estimating the molar fraction of water present, it has been assumed that the sucrose molecule is hydrated by four molecules of water. A fair agreement exists between the observed and the calculated partial pressures. Such agreement is to be expected since (*a*) the concentration of ester is in all cases small, so that, in so far as it affects the partial pressure of the water, Raoult's law should apply as a close approximation; (*b*) the observed vapour pressures of aqueous solutions of sucrose over a considerable range of sucrose content may be calculated fairly accurately from Raoult's law, assuming the above hydration.

Returning to the ester–water case, an interesting point arises when the observed values of p_e at various concentrations of ester are compared at the two temperatures 25° and 35°. The ratio $p_e(35°)/p_e(25°)$ decreases as the concentration or molar fraction of ester increases (see Table V). This means that the latent heat of vaporisation of ester from its aqueous solutions decreases with increasing molar fraction of ester. The same result is obtained if, with a constant concentration of ester, its molar fraction is

artificially increased by addition of sucrose. Table VI shows this decrease in the ratio $p_e(35°)/p_e(25°)$ with increasing sucrose content.

TABLE V.

Conc. of ester (mols. per litre).	$p_e(35°)/p_e(25°)$.
0·2542	1·70
0·5084	1·69
1·017	1·58
1·525	1·53
2·033	1·52
Pure ester.	1·53

TABLE VI.

(Constant conc. of ester = 0·2542*N*.)

Conc. of sucrose (g./litre).	$p_e(35°)/p_e(25°)$.
0	1·70
100	1·68
200	1·62
300	1·59

By applying the Duhem–Margules relation to the data of Table V, it readily follows that the ratio $p_w(35°)/p_w(25°)$ *increases* with increasing ester content, which in turn requires that the relative depression of the vapour pressure of the solvent water by addition of ester should be less the higher the temperature. This result is possibly of significance in relation to the evidence recently offered by Kendall and King (J., 1925, **127**, 1778) for the existence of an ester–water complex in aqueous solutions of ethyl acetate. If a similar complex were present in methyl acetate–water mixtures, increase of temperature would certainly favour its dissociation, and the relative depression of vapour pressure of the water would therefore decrease with increasing temperature. In this connexion might also be mentioned the appreciable contraction in volume accompanying the solution of methyl acetate in water.

Summary.

The partial vapour pressures of methyl acetate and water in ester–water and ester–sucrose–water mixtures have been determined at 25° and 35°.

The total vapour pressures of the same systems have been measured by an independent method at these temperatures.

The nature of the partial-pressure curves suggests appreciable compound formation between water and methyl acetate in aqueous solutions of the ester.

One of us (F. P. S.) desires to express his thanks to the Department of Scientific and Industrial Research for a maintenance grant during the course of this work.

MUSPRATT LABORATORY OF PHYSICAL AND ELECTROCHEMISTRY,
UNIVERSITY OF LIVERPOOL. [*Received, October 16th*, 1926.]

XVII.—*Organic Derivatives of Silicon. Part XXXII. The Carbon–Silicon Binding.*

By FREDERIC STANLEY KIPPING.

FRESH evidence is continually being obtained by the author that an ethylenic binding between carbon and silicon is either impossible or can only be produced under exceptional conditions. Those reactions which lead to the formation of an olefine seem to be quite inapplicable to the production of the group >Si:C<.

The loss of one molecule of water from one molecule of a tertiary silicol, $R_2Si(OH)\cdot CH_2R$, is an unknown change; under conditions which have not yet been fully investigated, such silicon compounds, instead of giving $R_2Si{:}CHR$, pass into the corresponding oxides, $(R_2Si\cdot CH_2R)_2O$, as, for example, in the cases of benzylethylpropylsilicol, $SiEtPr(CH_2Ph)\cdot OH$, and phenyldiethylsilicol, $SiEt_2Ph\cdot OH$. Many tertiary alcohols, on the other hand, are readily converted into olefines without any production of the corresponding ether.

Again, the loss of halogen acid from the molecule of a chloride, $R_2SiCl\cdot CH_2R$, has never been observed; such compounds can be distilled at relatively high temperatures without appreciable decomposition, as, for example, phenylethylpropylsilicyl chloride and tribenzylsilicyl chloride. This behaviour may be contrasted with that of many analogous carbon compounds which lose a molecule of halogen acid very readily, giving olefines; $CMeEt(CH_2Ph)Br$, for example, cannot be distilled even under low pressure. Similarly, many dichloro-derivatives, R_2SiCl_2, such as dibenzylsilicon dichloride distil at relatively high temperatures without decomposing.

The formation of an unsaturated compound by the action of a Grignard reagent on a tertiary silicyl chloride is also unknown; it has been proved in very many cases that a normal reaction occurs with the formation of a quaternary silicane, and, although by-products are nearly always obtained, these are substances of high boiling point; it is, of course, possible that these by-products are formed by the polymerisation of compounds containing the Si:C binding, but no evidence of this has been recorded. Many tertiary halogen derivatives, on the other hand, give rise to olefines (Trotman, J., 1925, **127**, 88) so readily that the formation of a saturated quaternary hydrocarbon either does not take place, or it does so only to a very limited extent.

Experiments with the direct object of producing the group >Si:C< seem to have been recorded in one instance only. Schlenk and Renning (*Annalen*, 1912, **394**, 221) treated silicon tetrachloride with magnesium phenyl bromide (2 mols.) in order to form

diphenyldichlorosilicane, and then heated the crude product with magnesium methyl iodide (1 mol.) in order to obtain diphenylmethylchlorosilicane; afterwards they decomposed this chloride with water and obtained by distillation a liquid boiling at 266—268°/72 mm. From the results of one combustion and a molecular-weight determination they assigned to this liquid the constitution $SiPh_2{:}CH_2$, although it did not react with bromine or with alkaline permanganate.

Now the known behaviour of certain pure silicols of an analogous structure (see above) casts grave doubt on this supposed conversion of diphenylmethylsilicol into an unsaturated compound.

Further, it is the author's experience that when silicon tetrachloride is treated with magnesium phenyl bromide (2—2½ mols.) the product is always a mixture, no matter how slowly the Grignard reagent is added, or whatever other precautions are taken to ensure the formation of the desired substance only. Consequently, since Schlenk and Renning did not purify either the dichloride, $SiPh_2Cl_2$, or the monochloride, $SiPh_2MeCl$, the final crude product must have been a complex mixture of silicon compounds (with diphenyl), from which it would be no easy task to isolate any component.

Schlenk and Renning's experiments have therefore been repeated, but all endeavours have failed to afford the slightest confirmation of their results.

Further attempts to prepare a compound containing the $>Si{:}C<$ group were then made; tribenzylsilicyl chloride was heated with quinoline or with dimethylaniline with the object of eliminating hydrogen chloride; apparently, however, no such change took place. Tribenzylsilicol, as was previously shown (J., 1909, **95**, 308), is unchanged when it is heated with acetic anhydride; further attempts to convert it into an unsaturated compound by heating it with phosphoric oxide or with zinc chloride have likewise given negative results.

Experimental.

To a solution of purified diphenyldichlorosilicane in ether (5 vols.) an ethereal solution of magnesium methyl iodide (1 mol.) was gradually added. There was very little heat developed, and no deposition of magnesium salt occurred, but after some time the liquid had separated into two liquid layers. The next day the ether was distilled, and the residue heated at about 120° during 2 hours; the magnesium salt had then become crystalline. The silicon compound was extracted from the magnesium salt in the usual way in the absence of moisture and was distilled (25 mm.) without fractionating in order to get rid of magnesium salt; a small proportion of a liquid of high boiling point remained in the residue. The whole distillate was then fractionated (45 mm.); it began to

boil at 170°, and from 170° to 185° a large fraction was collected. From 185° to 195° very little came over, but above this temperature a considerable proportion of diphenyldichlorosilicane was collected. The fractions 170—185° and 185—200° were separately redistilled many times, but no liquid of constant boiling point could be obtained. Analyses indicated that the portion boiling at 175—180° consisted chiefly of diphenyldimethylsilicane with some diphenylmethylsilicyl chloride; the latter compound was contained principally in the fraction 180—195°, a colourless, mobile liquid which fumed slightly in moist air.

In order to obtain a silicol the very impure chloride was diluted with light petroleum and shaken with either water or potassium hydroxide solution. The product distilled mainly from about 170—190° (45 mm.), and a little passed over up to about 210°, leaving a very small proportion of liquid of high boiling point, which was probably the oxide, but which could not be obtained in crystals; all attempts to isolate from the main fraction either the pure silicol or the unsaturated compound described by Schlenk and Renning were unsuccessful, and every time the liquid was distilled a very small proportion of the residue of high boiling point was formed. The combined fractions were then repeatedly distilled very slowly under atmospheric pressure; during each operation water was formed and a substance (the oxide) of high boiling point; after five such treatments, the distillate having been dried after each, the whole was put back on to the residue and the liquid was heated just below its boiling point during about 2 hours. Water was again formed and removed. Finally, the liquid was distilled (45 mm.); about 80% of the original preparation passed over from 165—185° and the thermometer then rose very rapidly to about 270°, above which temperature a thick, yellow oil was collected. The lower fraction did not decolorise a dilute chloroform solution of bromine, or an aqueous solution of permanganate; these facts, also observed by Schlenk and Renning with their preparation, afford strong evidence of the absence of unsaturated compounds. The higher fraction slowly deposited crystals of *diphenylmethylsilicyl oxide*, $(SiMePh_2)_2O$, which, freed from oil on porous earthenware, separated from cold alcohol in plates having the outline of a regular hexagon, or of a rhomb, and melting at 51—52° (Found: Si, 13·7. $C_{26}H_{26}OSi_2$ requires Si, 13·7%). This oxide is very readily soluble in ether, light petroleum (b. p. 50—60°), acetone, and other common solvents, from which it usually separates as an oil; it is only sparingly soluble in cold alcohol.

These results show that diphenylmethylsilicol is only very slowly decomposed when it is heated at its boiling point, and that, like

other silicols of a similar type, it then gives the oxide. Schlenk and Renning's product, obtained apparently after one distillation only, was doubtless a mixture of diphenyldimethylsilicane, diphenylmethylsilicol, and probably diphenyl, and the results of their single analysis can scarcely establish the existence of a compound containing the >Si·C< binding.

A pure specimen of *diphenyldimethylsilicane*, $SiMe_2Ph_2$, was prepared by treating diphenyldichlorosilicane with an excess of magnesium methyl iodide in ethereal solution, and then heating the residue at 150°; after cooling and addition of water, the silicon compound separated as an oil, and, on distillation, was obtained as a colourless, fairly mobile liquid with a faint aromatic odour, b. p. 176—178°/45 mm., and miscible with all organic solvents. It was not easy to estimate the silicon in this compound in the usual way, even using bromine or nitric acid in addition to sulphuric acid, all the results being low; good results, however, were obtained on combustion (Found: C, 79·0; H, 7·6. $C_{14}H_{16}Si$ requires C, 79·2; H, 7·5%).

The author is indebted to the Government Grant Committee of the Royal Society for a grant which covered a part of the cost of the materials, and also to Mr. J. E. Sands for assistance in some of the experimental part of this work.

UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, November 20th*, 1926.]

XVIII.—*Reactions of Carbohydrazide. Part I.*

By ANDREW CHARLES BROWN, ERIC CHARLES PICKERING, and FORSYTH JAMES WILSON.

As comparatively little work has been done on the aldehydic and ketonic derivatives of carbohydrazide, we decided, in conjunction with investigations on similar lines, to make a study of these compounds, particularly as regards their thermal decomposition.

The only such derivatives described so far are the dibenzylidene derivative, $CO(NH{\cdot}N{:}CHPh)_2$ (Curtius and Heidenreich, *J. pr. Chem.*, 1895, **52**, 471), and the dibenzophenone derivative, $CO(NH{\cdot}N{:}CPh_2)_2$, a compound tentatively described as such by Borsche and Merkwitz (*Ber.*, 1904, **37**, 3177; compare Wilson and Crawford, **J.**, 1925, **127**, 103), but not synthesised. We have prepared the following carbohydrazones from carbohydrazide and the appropriate ketone: *diacetonecarbohydrazone*, $CO(NH{\cdot}N{:}CMe_2)_2$, *di(methyl ethyl ketone)carbohydrazone*, $CO(NH{\cdot}N{:}CMeEt)_2$, *diacetophenonecarbohydrazone*, $CO(NH{\cdot}N{:}CMePh)_2$, and dibenzophenone-

carbohydrazone. By means of carbohydrazide, $CO(NH\cdot NH_2)_2$, we have prepared *carbohydrazones* of the type $CRR':N\cdot NH\cdot CO\cdot NH\cdot NH_2$ (which we designate *δ-aminosemicarbazones*) from benzaldehyde, acetophenone, benzophenone, benzil, and diacetyl; a compound of a mixed type, *benzaldehyde acetophenone carbohydrazone*, $CHPh:N\cdot NH\cdot CO\cdot NH\cdot N:CMePh$, has also been prepared. Acetylacetone and carbohydrazide gave 3 : 5-dimethylpyrazole.

The thermal decomposition of dibenzaldehydecarbohydrazone, diacetophenonecarbohydrazone, and benzaldehyde-δ-aminosemicarbazone occurred in two stages. In boiling absolute alcoholic solution, dibenzaldehydecarbohydrazone gradually underwent decomposition, giving dibenzaldehydehydrazidicarbohydrazone, already described by Stollé (*Ber.*, 1910, **43**, 2468), and benzylideneazine : $2CO(NH\cdot N:CHPh)_2 =$

$$CO(NH\cdot N:CHPh)\cdot NH\cdot NH\cdot CO(NH\cdot N:CHPh) + (CHPh)_2N_2.$$

When heated at its melting point, the carbohydrazone gave 4-aminourazole and benzylideneazine, the intermediate dibenzaldehydehydrazidicarbohydrazone evidently decomposing in this way : $CO(NH\cdot N:CHPh)\cdot NH\cdot NH\cdot CO(NH\cdot N:CHPh) =$ $NH_2\cdot N\!<\!\begin{matrix}\text{———}\\ CO\cdot NH\cdot NH\end{matrix}\!>\!CO + (CHPh)_2N_2$. Diacetophenonecarbohydrazone behaved in a similar manner, giving *diacetophenonehydrazidicarbohydrazone*, $CO(NH\cdot N:CMePh)\cdot NH\cdot NH\cdot CO(NH\cdot N:CMePh)$, and phenyl methyl ketazine in boiling alcoholic solution, and 4-aminourazole and phenyl methyl ketazine when heated without a solvent. Benzaldehyde-δ-aminosemicarbazone was scarcely affected in boiling alcohol; prolonged boiling in toluene solution gave hydrazidicarbohydrazide and benzylideneazine : $2CHPh:N\cdot NH\cdot CO\cdot NH\cdot NH_2 = NH_2\cdot NH\cdot CO\cdot NH\cdot NH\cdot CO\cdot NH\cdot NH_2 + (CHPh)_2N_2$. When heated a little above the melting point, the δ-aminosemicarbazone gave 4-aminourazole, hydrazine, and benzylideneazine, the former two compounds evidently resulting from the hydrazidicarbohydrazide :

$$NH_2\cdot NH\cdot CO\cdot NH\cdot NH\cdot CO\cdot NH\cdot NH_2 = NH_2\cdot N\!<\!\begin{matrix}\text{———}\\ CO\cdot NH\cdot NH\end{matrix}\!>\!CO + N_2H_4.$$

This work will be continued.

Experimental.

Carbohydrazide was prepared by Kesting's method (*Ber.*, 1924, **57**, 1323).

Diacetonecarbohydrazone (prisms from alcohol; m. p. 156°) was prepared by refluxing carbohydrazide with an excess of acetone for about 10 minutes and allowing the product to cool. Much heat was generated when the reactants were mixed (Found : N, 33·3. $C_7H_{14}ON_4$ requires N, 32·9%).

Di(methyl ethyl ketone)carbohydrazone (prismatic needles, m. p. 113°) was prepared in the same way, slightly more than 2 mols. of the ketone being used and the mixture being refluxed for only 5 minutes; the mixing of the reactants produced much heat. The almost solid product obtained on cooling was, after several hours, pressed on porous tile and then recrystallised from ether. The carbazone was readily soluble in acetone, alcohol, or water, and sparingly soluble in ether, and was rapidly hydrolysed by dilute mineral acids. This preparation was also carried out in aqueous solution, addition of potassium carbonate causing separation of the carbohydrazone (Found: N, 28·4. $C_9H_{18}ON_4$ requires N, 28·3%).

In the preparation of *diacetophenonecarbohydrazone*, the ease with which the derivatives decomposed in solution caused difficulties. 3 G. of carbohydrazide and 12 g. of acetophenone in 50 c.c. of absolute alcohol were gently heated for 1 hour; on cooling, the *carbohydrazone* (needles from aqueous alcohol; m. p. 204°) was deposited, but the yield was only 50% owing to decomposition during the working-up of the mother-liquor. The substance was sparingly soluble in cold solvents, but dissolved readily in hot water and in hot alcohol (Found: C, 69·2; H, 6·2; N, 19·2. $C_{17}H_{18}ON_4$ requires C, 69·4; H, 6·1; N, 19·0%).

3·2 G. of carbohydrazide and 4 g. of acetophenone in 50 c.c. of absolute alcohol gave, after being heated gently for 1 hour and then cooled, needles of carbohydrazide mixed with plates of *acetophenone-δ-aminosemicarbazone*. The latter compound (m. p. 188°) was isolated by dissolving out the carbohydrazide with cold water (Found: N, 29·0, 29·1. $C_9H_{12}ON_4$ requires N, 29·2%). The substance was readily soluble in hot water, alcohol, or pyridine and sparingly soluble or insoluble in other solvents.

Benzaldehyde acetophenone carbohydrazone (rhombic plates from alcohol; m. p. 160°) was obtained by refluxing 2 g. of the preceding compound and 1·5 g. of benzaldehyde in absolute alcohol for 1 hour and cooling the product. It dissolved in hot water, alcohol, benzene, and pyridine (Found: N, 19·3. $C_{16}H_{16}ON_4$ requires N, 20·0%).

Benzophenone reacted sluggishly. A solution of 1·8 g. of carbohydrazide and 3·64 g. of the ketone (1 mol.) in 10 c.c. of alcohol and 3 c.c. of water was refluxed for 7 hours, *benzophenone-δ-aminosemicarbazone*, $CPh_2{:}N{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NH_2$, being gradually deposited; after being washed with cold alcohol and with warm water, this crystallised from alcohol in glistening, diamond-shaped plates (yield, 75%), m. p. 223—224° (decomp.), which were slightly soluble in alcohol and insoluble in boiling water (Found: C, 66·2; H, 5·9; N, 22·0. $C_{14}H_{14}ON_4$ requires C, 66·1; H, 5·5; N, 22·0%).

An absolute alcoholic solution (40 c.c.) of 1·27 g. of this compound and 3 g. of benzophenone (large excess) was refluxed for 40 hours; the solution gradually became yellow, but even after this time the reaction was far from complete. On cooling, plates of the δ-amino-semicarbazone appeared followed by colourless needles of dibenzophenonecarbohydrazone. The latter, after fractional crystallisation from alcohol, melted at 222—223° (yield, 0·3 g.) (Found : C, 77·1; H, 5·5; N, 13·4. Calc. for $C_{27}H_{22}ON_4$: C, 77·5; H, 5·3; N, 13·4%) and was identical with the substance described by Borsche and Merkwitz (*loc. cit.*).

Benzaldehyde-δ-aminosemicarbazone was obtained by refluxing 5 g. of carbohydrazide and 4·5 g. of benzaldehyde in absolute alcohol for 1 hour and recrystallising from alcohol the product which separated on cooling; it formed lustrous plates, m. p. 173°, soluble in alcohol or chloroform (yield, good) (Found : N, 31·5. $C_8H_{10}ON_4$ requires N, 31·5%).

Benzilmono-δ-aminosemicarbazone, $COPh{\cdot}CPh{:}N{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NH_2$, was prepared by refluxing for ½ hour an absolute alcoholic solution of 5·8 g. of carbohydrazide and 13·5 g. (1 mol.) of benzil and then distilling off, during another ½ hour, most of the solvent. The almost solid mass obtained on cooling was washed with ether and recrystallised from absolute alcohol, white flakes, m. p. 172—174°, being obtained; these were slightly soluble in boiling alcohol and insoluble in benzene (Found : N, 19·2, 19·5. $C_{15}H_{14}O_2N_4$ requires N, 19·8%).

Diacetylmono-δ-aminosemicarbazone was prepared by heating on the water-bath molecular quantities of carbohydrazide and the diketone in absolute alcohol for 1 hour; the precipitate which gradually formed was collected hot and extracted twice with boiling absolute alcohol. The substance was a powder with a slightly yellow tinge, m. p. 260°, insoluble in all the usual solvents (Found : N, 35·3. $C_5H_{10}O_2N_4$ requires N, 35·4%).

An absolute alcoholic solution of acetylacetone (6 g.) and carbohydrazide (3 g.) was refluxed for 1 hour, and the solvent then evaporated. The residue, which slowly solidified, was dissolved in ether, recovered from the filtered solution, and dissolved in alcohol; slow evaporation then yielded a substance, m. p. 106—107°, which was identified as 3 : 5-dimethylpyrazole (Found : N, 29·1, 29·2. Calc. : N, 29·1%).

Thermal Decomposition of Carbohydrazones.

Dibenzaldehydecarbohydrazone.—An absolute alcoholic solution, on boiling for 24 hours, gradually became deep yellow. The solid deposited on cooling was collected, extracted with alcohol to dissolve

out unchanged substance, and then recrystallised from much alcohol; the needles, m. p. 228°, thus obtained were shown to be dibenzaldehydehydrazidicarbohydrazone by comparison with an authentic specimen and by analysis (Found: N, 26·0. Calc.: N, 25·9%). The original solution from which this substance had been removed contained benzylideneazine and a little unchanged substance; separation was effected by means of ether, in which the former alone was soluble.

On heating at 205° for 1 hour, the carbohydrazone formed an amber-coloured liquid. The cold melt, on extraction with ether, left a white residue which was recrystallised from water and then proved to be 4-aminourazole (mixed m. p. test). The ethereal solution contained benzylideneazine.

Diacetophenonecarbohydrazone.—An alcoholic solution was boiled for 26 hours. It soon became yellow and deposited a white precipitate, which was collected when cold. The filtrate contained phenyl methyl ketazine. Recrystallisation of the precipitate from alcohol gave a colourless, crystalline powder, m. p. 239—240° (yellow melt), which became grey on keeping. It was *diacetophenonehydrazidicarbohydrazone* (Found: N, 24·2. $C_{18}H_{20}O_2N_6$ requires N, 23·9%) and was only slightly soluble in hot alcohol, readily soluble in hot pyridine, and insoluble in other solvents even when hot.

The carbohydrazone, on heating at 220° for 50 minutes, gave an orange-coloured and ultimately dark brown liquid, ammonia being evolved. Extraction of the cold powdered melt with ether left a white residue which, after recrystallisation from water, melted at 269—270° and was identified as 4-aminourazole by a mixed melting-point test and by analysis (Found: N, 48·4. Calc.: N, 48·3%): the yellow ethereal solution contained phenyl methyl ketazine. The yield of these products was almost quantitative.

Benzaldehyde-δ-aminosemicarbazone.—Scarcely any reaction occurred in boiling alcoholic or benzene solution. Boiling in toluene solution, however, for 31 hours effected decomposition. The white precipitate produced was collected when cold; after recrystallisation from absolute alcohol it melted at 197° and was identified as hydrazidicarbohydrazide (Stollé, *Ber.*, 1910, **43**, 2469). The toluene filtrate contained benzylideneazine.

The δ-aminosemicarbazone, on heating at 175° for 1½ hours, gave a deep yellow liquid, hydrazine, recognised by its reducing action, and ammonia being evolved. Extraction of the cold powdered melt with ether left a residue which, after recrystallisation from aqueous alcohol and then from water, melted at 270° and was identified as 4-aminourazole by comparison with an authentic specimen. The ethereal solution contained benzylideneazine.

Our thanks are expressed to Messrs. A. M. Munro, A. D. Neilson, B.Sc., and W. B. Stewart, B.Sc., for experimental assistance. We wish also to thank the Carnegie Trust for the Universities of Scotland for a research grant in aid of this work.

THE ROYAL TECHNICAL COLLEGE,
GLASGOW. [*Received, September 23rd,* 1926.]

XIX.—*The Vapour Pressure of Water over Sulphuric Acid–Water Mixtures at* 25°.

By IVAN ROY MCHAFFIE.

THE present investigation was carried out to test the accuracy of a method of measuring very small amounts of water vapour, present in air, employed by the author in another research. It was thought that this could be attained by measuring the vapour pressure of water over sulphuric acid–water mixtures of fairly high concentration. The results did not agree with the data relating to 25° given in the Landolt–Börnstein tables, but were in good agreement among themselves and with those of other workers. As sulphuric acid–water mixtures are frequently used for controlling the amount of water vapour present in air, the results may prove of interest.

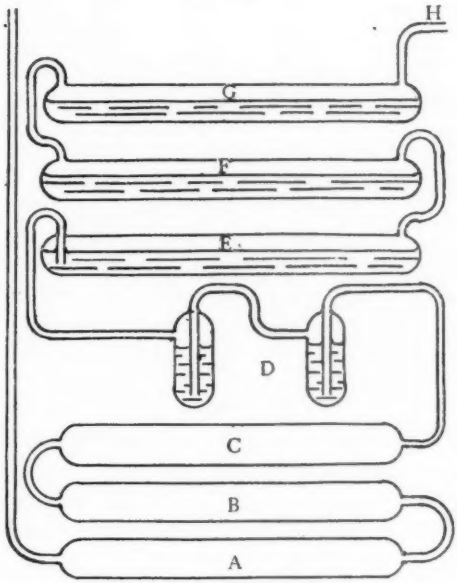
The method of measuring small amounts of water vapour present in " permanent " gases has been described elsewhere (*J. Amer. Chem. Soc.*, 1926, **48**, 1143) and is briefly as follows. The water vapour from a known volume of air is frozen out, by means of liquid air, in a condensation tube of known volume to which a mercury manometer is attached. The air is then removed from the condensation tube, still maintained at the temperature of liquid air, by mercury-diffusion vacuum pumps. The temperature of the condensation tube is then raised until all the water frozen out has been converted into vapour. The pressure of this water vapour at a known volume is then read off; hence it is possible to calculate the mass of water present.

The system of saturators is shown in Fig. 1. The tube A was filled with soda-lime, B with phosphorus pentoxide, and C with a mixture of hydrated and anhydrous oxalic acid. The bubblers, D, and the tubes, E, F, and G, contained the sulphuric acid–water mixtures. H was connected to the condensation tube, which was in turn connected to an aspirator bottle and the necessary evacuating apparatus. The volume of the portion of the apparatus containing the sulphuric acid–water mixtures was 500 c.c., half of which was filled with the mixtures. The greater amount of the spray produced

in the bubblers, D, would settle out in the tubes E, F, and G; also at rates of flow varying from 1 to 4 litres per hour no change in the value of the vapour pressure at any one concentration of the mixture was observed. For these reasons, the insertion of a spray filter at the end of the saturator was considered to be unnecessary. The portion of the apparatus shown in Fig. 1 was immersed in a water thermostat maintained at 25°.

At each concentration measurements were made both with and without the tube C in the saturating system; thus equilibrium was

FIG. 1.



reached with air containing both a higher and a lower concentration of water vapour than that in equilibrium with the sulphuric acid–water mixtures. At the highest concentration of sulphuric acid, each successive determination was lower than the previous one. The value given for this concentration in the following table is the first one obtained and has a probable error of 0·01 mm. The explanation of this appears to be that, with mixtures at this concentration, there is an appreciable vapour pressure of sulphuric acid as well as water vapour in the gas phase. Consequently sulphuric acid as well as water vapour would collect in the condensation tube and the pressure measured would be too low. This accumulation of sulphuric acid will not be totally removed by the evacuating pumps, during the preliminary drying of the condensation

tube, hence each reading will be lower than the preceding one. This effect cannot be due to the presence of sulphur dioxide as an impurity in the sulphuric acid, as this would tend to give too high rather than too low a result.

Results.—The readings obtained in the series of measurements at 25° are in Table I.

TABLE I.

% H_2SO_4.	$T_{asp.}$.	V (c.c.).	p_b.	P_{H_2O}.	T_u.	p.	Vap. press. (mm. Hg).
65·9	15·5°	200	760·7	11·5	34·4°	15·90	1·803
65·9	15·6	275	754·5	11·5	41·0	22·15	1·789
76·0	16·3	400	747·5	12·5	17·8	5·00	0·301
76·0	17·0	600	748·4	11·0	17·8	7·33	0·295
76·0	16·3	1800	743·4	11·5	39·0	23·54	0·294
79·4	16·0	2000	745·3	12·0	31·1	13·74	0·158
83·5	17·5	5000	759·9	14·0	38·8	18·08	0·082

(The volume of the condensation tube was 23·73 c.c.)

The first column gives the proportion of sulphuric acid present in the mixtures; $T_{asp.}$ is the temperature of the aspirator; V, the number of c.c. of air passed through the apparatus; p_b, the barometric pressure; P_{H_2O}, the pressure of the water manometer attached to the aspirator; and T_u is the temperature of the condensation tube at which the pressure p, due to water vapour, was read. The last column gives the vapour pressure (in mm. Hg) calculated from the data by the expression

$$23{\cdot}73pB_{sat.}T_{asp.}/VT_uB_{asp.},$$

in which the temperatures are expressed as degrees absolute; $B_{sat.}$ is the pressure of the air within the saturator, *i.e.*, p_b corrected for P_{H_2O}; $B_{asp.}$ is the pressure of the air within the aspirator, *i.e.*, p_b corrected for P_{H_2O} and for the vapour pressure of water at the temperature $T_{asp.}$.

Brönsted (*Z. physikal. Chem.*, 1910, **68**, 708) (compare Lewis and Randall, "Thermodynamics," p. 331) has carried out similar measurements employing a modified tensimeter. The vapour pressures obtained by him, at the corresponding concentrations, are shown in Fig. 2.

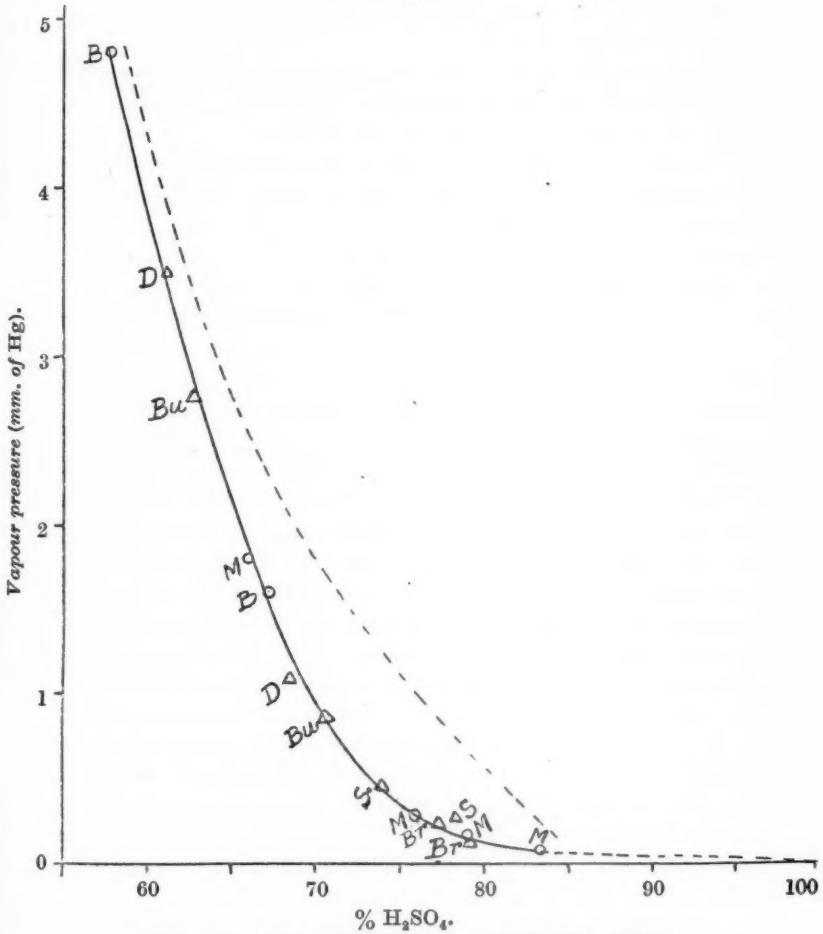
Wilson (*Ind. Eng. Chem.*, 1921, **13**, 4, 326) has calculated the vapour pressures of these mixtures at 25° from the data of various workers obtained at 0° and 100°, by means of the equation

$$\log (r_2/r_1) = \Delta H_2(T_2 - T_1)/2{\cdot}3RT_1T_2,$$

where r_1 and r_2 are the ratios of the vapour pressures of the mixtures to those of pure water at the temperatures T_1 and T_2, and ΔH_2 is the heat absorbed when 1 mole of water is removed from the solution without change in concentration. The value of ΔH_2 used was

always that for the mean between the particular T_1 and T_2 involved. These calculated values are shown in Fig. 2; the investigator upon whose data they were based is named. The values found in the present investigation are also shown. The values from the Landolt–

FIG. 2.



○ *Experimentally determined.* △ *Calculated by Wilson.*

B Brönsted; D Dieterici; Bu Burt; Br Briggs; S Sorel; M McHaffie.

Börnstein tables at 25° are represented by the broken curve. There is very good agreement between the calculated values of Wilson, the experimental values of Brönsted, and those of the present investigation. This would tend to show that the values obtained for the vapour pressure of water over sulphuric acid–water mixtures are

correct, and also that the method of measuring small amounts of water vapour is trustworthy when the pressure of water vapour is as low as 0·08 mm.

Summary.

(1) The vapour pressure of water over sulphuric acid–water mixtures at 25° has been measured for mixtures containing from 66 to 84% of sulphuric acid.

(2) These results agree with the experimental values obtained by Brönsted and with those calculated by Wilson, but not with the data for 25° in the Landolt–Börnstein tables.

(3) The method employed in the present research for measuring small amounts of water present in air has been found trustworthy for pressures as low as 0·08 mm.

THE SIR WILLIAM RAMSAY LABORATORIES OF
PHYSICAL AND INORGANIC CHEMISTRY,
UNIVERSITY COLLEGE, LONDON. [*Received, October 28th,* 1926.]

XX.—*Cyclic Organo-metallic Compounds. Part III. Nitro- and Amino-derivatives of Phenoxtellurine.*

By HARRY DUGALD KEITH DREW and REUBEN WILLIAM THOMASON.

IN the thiazines and oxazines, of which methylene-blue and Meldola's blue are examples, respectively, the central ring contains the odd-valent element nitrogen, together with sulphur or oxygen. In phenoxtellurine, nitrogen is replaced by the even-valent element tellurium. Having regard, therefore, to the uncertainty which still prevails as to the distribution of bonds in the coloured salts of the first-mentioned series, it was considered desirable to investigate the properties of the amino-derivatives of phenoxtellurine (I) from the point of view of possible colour-development among their salts. For, in that event, the coloured substances of the phenoxtellurine series must of necessity consist of dimeric molecules, or must contain each an extra acid radical, in order to simulate the structures ascribed to methylene-blue and the like.

An attempt to condense 2-nitrodiphenyl ether with tellurium tetrachloride led to profound decomposition, phenolic substances being produced. Since, in addition, the condensation of amino-compounds with tellurium tetrachloride is generally unfavourable, it was decided to prepare the aminophenoxtellurines by direct nitration of phenoxtellurine, followed by reduction of the nitro-compounds. This method proved practicable.

When phenoxtellurine is treated with nitric acid, it is first

quantitatively transformed by an oxidising reaction to the 10 : 10-dinitrate. Under suitable conditions, this action is then followed by nitration of the nucleus. Nitro-dinitrates, or nitro-basic-nitrates, of phenoxtellurine are thus produced; and these, on reduction by alkali bisulphite, are quantitatively transformed to nitro-derivatives of phenoxtellurine. The latter can then be reduced, by means of tin and hydrochloric acid, to the corresponding amino-derivatives.

Treatment of phenoxtellurine with ordinary concentrated nitric acid (*d* 1·42) leads chiefly to the formation of mononitro-derivatives, the main product consisting of 2-*nitrophenoxtellurine* (II), the by-product being 4-*nitrophenoxtellurine* (III).

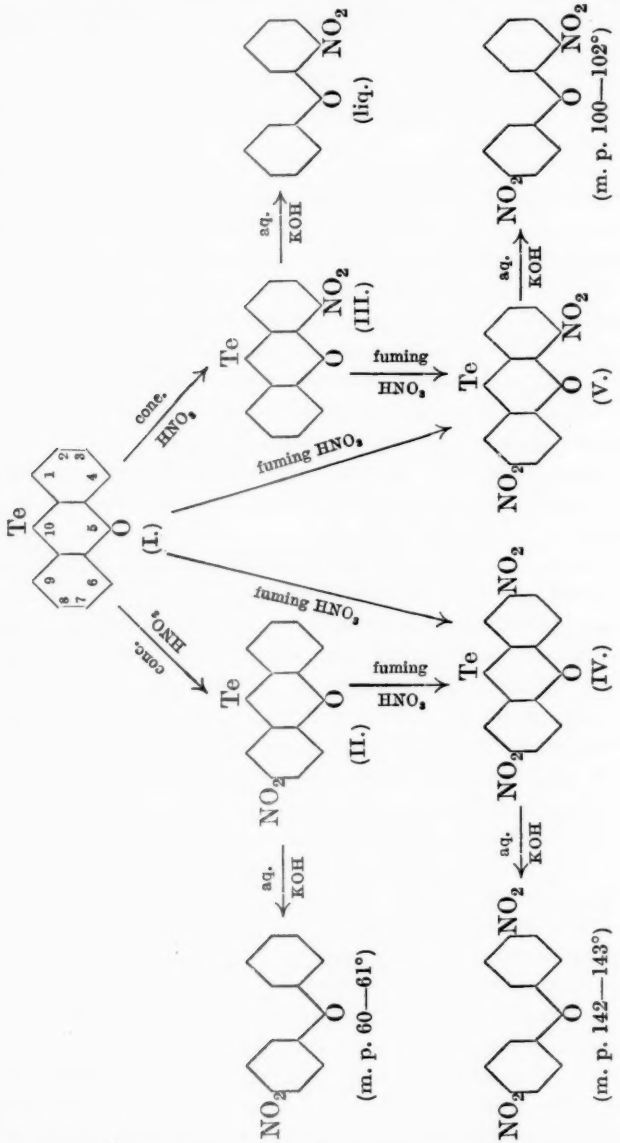
By the use of boiling fuming nitric acid, a second nitro-group is caused to enter the nucleus, and there are obtained, after reduction of the salts, 2 : 8-*dinitrophenoxtellurine* (IV) as main product and 4 : 8-*dinitrophenoxtellurine* (V) as by-product. A small proportion of 4 : 6-dinitrophenoxtellurine is doubtless also produced, but this substance has not yet been isolated.

The phenoxtellurine nucleus offers considerable resistance to further nitration, and tri- or higher nitro-derivatives were not obtained.

The nitro- and dinitro-phenoxtellurines are well-crystallised, yellow to orange-red substances, soluble in organic solvents, and possessed of considerable stability. The proof of the orientation of the nitro-groups therein was supplied in a simple manner by extending to these compounds the observation previously made, in the case of phenoxtellurine itself, that the 10 : 10-dichlorides, -dinitrates, and other similar salts are decomposed by warm aqueous potash in a manner leading to replacement of the tellurium atom by two atoms of hydrogen, potassium tellurite and the appropriate substitution product of diphenyl ether being generated in each case. Identification of the latter affords unequivocal information as to the structure of the phenoxtellurine derivative itself, except when substituents are present in positions relatively *meta-* to the ether oxygen atom (*i.e.*, in positions 1, 3, 7, or 9). So far, no such doubtful cases have been encountered. Inspection of the formulations given below will make clear the foregoing argument.

The nitrodiphenyl ethers produced from (II), (IV) and (V) by the action of potash were known crystalline substances having characteristic melting points, and the methods by which they have already been synthesised leave no doubt regarding their structure. The 2-nitrodiphenyl ether resulting from (III), however, is a liquid. The proof of the orientation of the nitro-group was therefore supplied by further nitration to (V). Confirmation of the struc-

ture of (II) was obtained by similar further nitration to (IV). The following scheme illustrates the methods employed :



The separation of the nitro-derivatives of phenoxtellurine is complicated by the existence of a series of addition compounds between the various members. Some of these occur in well-defined

crystals of characteristic appearance; and repeated crystallisation from certain organic solvents fails to disrupt them, although other solvents effect complete or partial separation into the constituent substances. In the cases observed, a molecule of each of two nitro-derivatives may be combined; or two molecules of one derivative may unite with a single molecule of a second. Thus, two molecules of (IV) unite with a molecule of (II) to form a complex crystallising from acetone in orange-red prisms; whilst a molecule of (IV) unites with a molecule of (II) to form a complex separating from alcohol in yellow, hexagonal plates. Phenoxtellurine itself unites with a molecular proportion of 2-chloro-8-methylphenoxtellurine to form a remarkable *compound*, which crystallises unchanged, from petroleum or ethyl alcohol, in well-defined, yellow needles having a perfectly sharp melting point. This substance is always found associated with phenoxtellurine when the latter is prepared from ordinary (solid) diphenyl ether and tellurium tetrachloride, owing, we are of an opinion, to the presence of *p*-cresol in the material from which the diphenyl ether is made.

That these additive compounds are not the result of union between the bivalent tellurium atoms of several molecules is indicated by the fact that the corresponding complex 10 : 10-dichlorides and dinitrates, containing only quadrivalent tellurium, may in some cases be recrystallised substantially unchanged.

A point of interest emerging from the study of the nitration of phenoxtellurine is that the orienting influence of the tellurium atom, in the form of the group $>Te(NO_3)_2$, on the entering nitro-groups is negligible in comparison with that of the ether oxygen atom, unless, indeed, the telluridinitrate group be considered *meta*-directive, in which case the separate influences of the two directive groups would be reinforcing. As would be expected, the entry of a second nitro-group into the phenoxtellurine ring occurs mainly, if not exclusively, in the unnitrated phenylene group.

Incidentally, the results afford confirmation of the structure of phenoxtellurine itself, since they indicate that the tellurium and oxygen atoms in that substance are attached to the phenylene groups in mutually di-*ortho*-positions.

The foregoing nitro-derivatives are readily reduced by means of tin and hydrochloric acid, 2-*amino*-, 2 : 8-*diamino*-, and 4 : 8-*diamino-phenoxtellurine* being thus produced. These substances are crystalline, stable, and appreciably soluble in water. Their hydrochlorides are readily diazotised or tetrazotised, giving yellow to red diazonium salts which may be coupled with reactive phenols, etc., to produce azo-dyes and pigments. The amines themselves have no special bactericidal action.

The action of boiling aqueous potash or soda upon the amines replaces tellurium by two atoms of hydrogen, yielding the corresponding amino-derivatives of diphenyl ether. From the latter, the amino-substituted phenoxtellurines are sharply distinguished by their instant action upon phenoxtellurine dibisulphate, mere traces of the telluride and the phenoxtellurine salt sufficing to produce, when rubbed together, the brilliant violet colour characteristic of diphenoxtellurylium salts (J., 1926, 3054).

Examination of the foregoing organic derivatives of tellurium, several of which have been carefully fractionated and repeatedly analysed, has yielded no evidence that tellurium is a complex (compare Brauner, J., 1895, **67**, 549). On the contrary, the results point to the probability that the accepted atomic weight for tellurium represents that of a single element (mixture of isotopes).

Experimental.

Complex By-product in the Preparation of Phenoxtellurine.—When 183 g. of tellurium tetrachloride were condensed with diphenyl ether in the manner previously described (*loc. cit.*), 178 g. of crude 10 : 10-dichlorophenoxtellurine were obtained. This, when reduced without further purification, yielded 14 g. of free tellurium, 80 g. of pure phenoxtellurine, and 20 g. of a complex by-product which closely resembled phenoxtellurine in general properties. The by-product was separated from phenoxtellurine by crystallisation from light petroleum (b. p. 40—60°), remaining in the first mother-liquor. Subsequent purification was effected from ethyl alcohol. A complete separation of these two substances is obtained with surprising ease.

The *by-product* is a compound of a molecule of phenoxtellurine with one molecule of 2(?)-chloro-8(?)-methylphenoxtellurine. It results from the presence in the diphenyl ether of a small proportion of phenyl *p*(?)-tolyl ether, which is chlorinated by tellurium tetrachloride, the product becoming transformed into 2(?)-chloro-8(?)-methylphenoxtellurine, which then unites with phenoxtellurine. It separates from ethyl or methyl alcohol, or from petroleum, in bushes of well-defined, light yellow needles with chiselled ends, and melts sharply at 59°. Conversion into the dinitrate by means of dilute nitric acid does not effect resolution of this substance into its constituents, since it is recovered unchanged on reduction of the recrystallised product. Partial separation may be obtained, however, by repeated fractionation of the 10 : 10-dichloride from chloroform. Nucleus nitration results in disintegration of the complex, nitro-derivatives of phenoxtellurine becoming isolable. In benzene solution, the compound is com-

pletely resolved into its constituents, although it is reformed when the solution is concentrated [Found : *M* (cryoscopic), 284, 287, 295. Calc., *M*, 319·8].

Mixtures of the complex substance with phenoxtellurine melt indefinitely between 59° and 79°. Removal of tellurium, by boiling with aqueous potash, gave a heavy oil which contained diphenyl ether but did not solidify. This was probably a mixture of diphenyl ether with *p*-chlorophenyl *p*-tolyl ether [Found : C, 47·05, 47·0; H, 2·9, 2·7; Cl, 5·3, 5·4; TeO, 44·9 (by diff.). $C_{25}H_{17}O_2ClTe_2$ requires C, 46·9; H, 2·65; Cl, 5·55; TeO, 44·9%]. For comparison, analyses were carried out on specimens of phenoxtellurine prepared in the same experiment (Found : C, 48·6, 48·8, 48·5; H, 2·9, 2·85, 2·8. $C_{12}H_8OTe$ requires C, 48·7; H, 2·7%).

Nitration of Phenoxtellurine.—(1) *Preparation of mononitrophenoxtellurines.* Powdered phenoxtellurine (4·5 g.) was added slowly to 70 c.c. of nitric acid (*d* 1·42), and the orange-red solution obtained after 10 minutes' boiling yielded, after 2 days, opaque, white needles (5·7 g., after being dried over soda-lime). The mother-liquor, concentrated on the water-bath, yielded further solid (0·9 g.) which, on reduction, gave chiefly 2 : 8-dinitrophenoxtellurine.

The main crop (5·7 g. above), when reduced by 30 c.c. of water and 5·7 g. of potassium metabisulphite, was transformed into a dark paste. The yellow ethereal extract of this, when allowed to evaporate on a wide surface, left yellow needles (A) surrounded by orange-red flakes (B). These two products were separated mechanically and each was crystallised from acetone. The orange-red flakes (B) gave slender, yellow crystals of 2 : 8-dinitrophenoxtellurine, together with massive, red prisms melting gradually from 145° to 220°. The latter substance was a *compound* containing two molecular proportions of 2 : 8-dinitrophenoxtellurine and one proportion of 2-nitrophenoxtellurine, into which it was separated by fractionation from ethyl alcohol (Found : N, 6·0. $C_{36}H_{19}O_{13}N_5Te_3$ requires N, 6·3%). From acetone, the complex could be recrystallised almost unchanged.

The yellow needles (A) gave a first crop of crystals, part of which dissolved more readily than the remainder in hot ethyl alcohol. The soluble portion separated from alcohol in silky, bright yellow needles of 2-*nitrophenoxtellurine* (II), m. p. 129° (Found : C, 42·2; H, 2·25; N, 4·25. $C_{12}H_7O_3NTe$ requires C, 42·3; H, 2·05; N, 4·1%). The less soluble portion separated from hot alcohol in glistening, bright yellow spangles, consisting of thin, hexagonal prisms. This substance was a *compound* of 2 : 8-dinitro- and 2-nitro-phenoxtellurines in molecular proportion (Found : N, 5·7. $C_{24}H_{13}O_8N_3Te_2$ requires N, 5·8%). The complex could be recrystallised unchanged

from alcohol, but was partly disrupted by acetone. It melted gradually between 145° and 185°.

The acetone mother-liquor from A, allowed to evaporate very slowly, gave small, yellow needles of impure 2-nitrophenoxtellurine, together with massive, lemon-yellow prisms. The prisms, sorted out by hand and recrystallised from ethyl alcohol, gave pale lemon-yellow prisms or needles of 4-*nitrophenoxtellurine* (III), m. p. 104° (Found : C, 42·4; H, 2·2; N, 4·2%).

(2) *Preparation of dinitrophenoxtellurines.* Powdered phenoxtellurine (4·3 g.) was added gradually to 25 c.c. of nitric acid (*d* 1·50), cooled in ice and salt. The mixture was then heated on a water-bath during ½ hour. The cooled solution was precipitated by addition of water and the white solid was removed and recrystallised from boiling nitric acid (*d* 1·42). The first crop (3·9 g.), when crystallised again from nitric acid, gave large, colourless, serrated needles (2·9 g.) which, on reduction with aqueous potassium metabisulphite, yielded pure 2 : 8-*dinitrophenoxtellurine* (IV), m. p. 228°. This substance crystallised from acetone in large, hexagonal, orange prisms, or from ethyl alcohol in smaller, yellow prisms. It was more sparingly soluble in organic solvents than the foregoing mononitrophenoxtellurines (Found : C, 37·9; H, 1·85; N, 7·3. $C_{12}H_6O_5N_2Te$ requires C, 37·4; H, 1·55; N, 7·3%).

The nitric acid mother-liquor from the above first crop was diluted with water and the white precipitate (4·2 g.) was boiled with 20 c.c. of fuming nitric acid during 2 hours. Precipitation by water and crystallisation of the precipitate from concentrated nitric acid gave a further crop of the above serrated needles. The nitric acid mother-liquor from this crop slowly deposited a second substance in minute, white rods. This, after recrystallisation in a similar manner from concentrated nitric acid, yielded, on reduction with aqueous potassium metabisulphite, pure 4 : 8-*dinitrophenoxtellurine* (V), m. p. 197—198°. This substance crystallised from benzene in long, thin, golden, lath-like needles containing $\frac{1}{2}C_6H_6$ (Found : loss of benzene at 100°, 9·2. Calc., 9·3%). The benzene was slowly lost in the air, the dinitro-compound remaining as a salmon-red, crystalline powder (Found : C, 37·0; H, 1·9; N, 7·3%). The substance separated from ethyl alcohol in minute, red crystals. It was generally only sparingly soluble in organic solvents.

Although the basic nitrate of 4 : 8-dinitrophenoxtellurine is much less easily soluble in nitric acid than is the dinitrate of 2 : 8-dinitrophenoxtellurine, the former tends to remain in supersaturated solution while the latter crystallises readily.

Many other experiments on the nitration of phenoxtellurine with nitric acid under a variety of conditions led to the conclusion

that the reaction cannot be controlled so as to produce mononitro-compounds only, lesser proportions of dinitro-compounds invariably being present. On the other hand, conditions are readily chosen in which only dinitro-compounds are produced. Fuming nitric acid, at atmospheric pressure, seems to be incapable of introducing more than two nitro-groups into the phenoxtellurine nucleus. Nitration in presence of auxiliary acids has not yet been tried.

Nitration of 2-Nitrophenoxtellurine.—A solution of 2-nitrophenoxtellurine in fuming nitric acid was boiled during 2½ hours. Separation of the products in the manner already described yielded crystals which, on reduction, gave pure 2 : 8-dinitrophenoxtellurine. The mother-liquor contained a substance which furnished, on reduction, a mixture of 2 : 8- and 4 : 8-dinitrophenoxtellurine. The latter, present only in very small proportion, was not isolated but was characterised by its colour change on crystallisation from benzene and exposure of the crystals to air.

Nitration of 4-Nitrophenoxtellurine.—Finely powdered 4-nitrophenoxtellurine (0·4 g.) was added slowly to cold fuming nitric acid (5 c.c.). The solution was boiled during 2 hours, and water was then added until a turbidity appeared. The white solid which subsequently separated was reduced with aqueous potassium metabisulphite, furnishing, after crystallisation from benzene, pure 4 : 8-dinitrophenoxtellurine (V), m. p. 198°, in 60% yield. The mother-liquor contained another nitro-compound, probably 4 : 6-dinitrophenoxtellurine, but the proportion was too small to allow of its isolation.

Conversion of Nitro-derivatives of Phenoxtellurine into Nitro-derivatives of Diphenyl Ether.—2-Nitrophenoxtellurine was converted into its dinitrate by means of nitric acid, and the crystals were boiled for a few minutes with 50% aqueous potash. Extraction by a mixture of ether and benzene furnished a solid which, after one crystallisation from ethyl alcohol, gave 4-nitrodiphenyl ether in very pale yellowish-white, flat plates, m. p. 60—61°.

4-Nitrophenoxtellurine was converted into its 10 : 10-*dibromide* (pale yellow crystals, melting and decomposing at 302°), which was then boiled with 30% aqueous potash. Extraction with ether gave *o*-nitrodiphenyl ether, a pleasant-smelling oil which did not solidify on keeping.

2 : 8-Dinitrophenoxtellurine, similarly converted into its dinitrate and boiled with 30% aqueous potash, yielded a solid which, after one crystallisation from alcohol, gave pale yellowish-white needles of 4 : 4′-dinitrodiphenyl ether, m. p. 142—143°.

4 : 8-Dinitrophenoxtellurine was converted into the basic nitrate,

and the latter boiled with 50% aqueous potash for a few minutes; the mixture was diluted with an equal bulk of water and then further heated at 100° for an hour. Extraction with much benzene gave 2 : 4′-dinitrodiphenyl ether, large, brittle, glassy, brownish prisms, m. p. 100—102°, from alcohol.

Amino-derivatives of Phenoxtellurine.—*2-Aminophenoxtellurine.* Finely powdered 2-nitrophenoxtellurine (2 g.) was heated on a water-bath during several hours with a large excess of tin and concentrated hydrochloric acid, until the yellow colour of the nitro-compound had disappeared. After filtration, the solid and filtrate were treated separately with cold caustic soda solution, and the liberated amine was extracted with chloroform in a Soxhlet apparatus. The amine was converted into the hydrochloride, which crystallised from water in small, very pale yellow needles. The addition of caustic soda to this solid gave *2-aminophenoxtellurine*, which crystallised from aqueous alcohol in pinkish-white needles, m. p. 157° (Found: N, 4·65. $C_{12}H_9ONTe$ requires N, 4·5%). Proof of orientation of this amine was shown by boiling it with aqueous potash, 4-aminodiphenyl ether (colourless needles from alcohol; m. p. 84°) being obtained.

By diazotising 2-aminophenoxtellurine at 0°, a pale yellow solution was obtained; and this, on coupling with alkaline β-naphthol, gave an insoluble, red azo-dye.

2 : 8-*Diaminophenoxtellurine.*—Finely ground 2 : 8-dinitrophenoxtellurine (3·8 g.) was heated with tin and concentrated hydrochloric acid on the water-bath, the red powder gradually becoming yellow; it was necessary to decant the clear liquid occasionally and grind the solid. The sparingly soluble hydrochloride of the amine was collected and treated with caustic soda. The amine thus formed was filtered off and extracted with chloroform, the cooled extract yielding 2 : 8-*diaminophenoxtellurine*, which crystallised from alcohol in lemon-yellow needles, m. p. 198° (Found: C, 44·3; H, 3·05; N, 8·6. $C_{12}H_{10}ON_2Te$ requires C, 44·2; H, 3·05; N, 8·6%). This diamine is slightly soluble in water and yields a hydrochloride which crystallises from hot water in long, yellow needles. Tetrazotisation causes the formation of a blood-red solution which yields an insoluble red azo-dye with alkaline β-naphthol.

4 : 8-*Diaminophenoxtellurine.* When 4 : 8-dinitrophenoxtellurine was similarly treated with tin and hydrochloric acid, the reduction proceeded much more rapidly. After the orange colour had disappeared, the hydrochloride was separated and crystallised from water. The action of caustic soda liberated 4 : 8-*diaminophenoxtellurine*, which crystallised from aqueous alcohol or water in faintly yellow, feathery needles or mica-like plates, m. p. 156° (Found:

C, 44·15; H, 3·0; N, 8·65%). On tetrazotisation, the diamine yielded a bright red diazonium chloride, which formed a red azo-dye with alkaline β-naphthol.

UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

[*Received, November 12th*, 1926.]

XXI.—*Anticathodic Luminescence of some Organic Substances.*

By JOSEPH KENNETH MARSH.

WHEN organic substances are cooled and bombarded with cathode rays there is very frequently an emission of light of greater or less intensity. This phenomenon was first extensively studied by Goldstein (*Verh. deut. physikal. Ges.*, 1904, **6**, 156). Later a study was made by O. Fischer (*Z. wiss. Phot.*, 1908, **6**, 305) of a number of substances which gave discontinuous spectra. From his work, it is evident that there is usually some degree of regularity in the position of the bands given by each substance, and Baly (*Phil. Mag.*, 1915, **29**, 223) and Henri ("Etudes de Photochimie," 1919) have both found support for their theories with regard to the relationship of infra-red and ultra-violet spectra from the positions of the anticathodic luminescence bands.*

The present work was undertaken in the hope that some further information might be gained as to the origin and significance of the anticathodic glow. Visual observations were made of a large number of organic substances, but in the great majority of cases the glow was too feeble to admit of photography, and also it was often continuous in character. Goldstein distinguished three different spectra which it was possible for one substance to exhibit, *viz.*, an initial spectrum, the chief spectrum, and a solution spectrum. The present investigation has been confined to pure substances, so that it is not concerned with solution spectra. All the substances examined showed a partial loss of luminescent power after a few minutes or even seconds of bombardment. This was due in part to the fading of the initial spectrum. Partial recovery sometimes occurred after an interval of rest, but some of the loss of luminescent power was due to a surface decomposition of the material. The initial spectrum was usually of greatest interest, as it sometimes consisted of distinct, bright bands; these gradually diffused them-

* These spectra have usually been termed cathodo-luminescence, but are produced when the materials act as anticathodes in a discharge tube, and so the term anticathodic luminescence would seem to be more fitting,

selves into a continuous spectrum—the chief spectrum of Goldstein. A phosphorescence lasting often for a minute or more was frequently seen on stopping the bombardment. This sometimes gave a spectrum which consisted of the same bands as were observable during the bombardment and, like the initial spectrum, decreased after a period of excitation.

A discharge tube similar in type to that used by Fischer was employed, and liquid air was used for cooling. In some cases, the glow, and likewise the phosphorescence, was stronger at temperatures higher than that of liquid air. There was also the disadvantage that the liquid exhibited several absorption bands across the usual range of the anticathodic luminescence spectrum, but, on the other hand, it enabled rather volatile substances to be examined. A small silica vacuum cup with an unsilvered patch held the liquid air into which the end of the discharge tube dipped. The spectrograph was a two-prism glass instrument giving a bright visible spectrum about 5 cm. long.

The materials examined fall into four classes, giving, respectively, (1) little or no glow, (2) a continuous spectrum only, although often of a distinctive hue, (3) a glow identifiable with the fluorescence spectrum, and (4) a distinctive banded spectrum.

(1) Those giving little or no spectrum include fully saturated compounds, nitro-compounds, strongly coloured substances, aldehydes, etc.; the following substances were found to belong to this class: hexane, paraffin wax, oleic acid, dipentene, bisdiphenyleneethylene, carbon tetrachloride, * hexachloroethane, nitrobenzene, *m*-nitroanisole, *o*-nitrophenol, benzaldehyde, cinnamaldehyde, quinone, quinol, 1 : 2-naphthaquinone, diphenyl ether, acridone, azobenzene, rosaniline, *p*-anisidine, benzaldoxime, and quinoline.

(2) A continuous spectrum was furnished by the following substances. The glow was most often blue or violet to the naked eye. Other colours are recorded in brackets after the substance. Stilbene, tolane, phthalic acid, terephthalic acid, *p*-hydroxybenzoic acid, phenol (green), *p*-cresol (green), fluorenone (green), coumarin, benzonitrile, *p*-chloroaniline, *p*-chlorobenzaldehyde, ethyl *p*-aminobenzoate (white), acridine (green), phenazone, sodium naphthionate, methyl propyl ketone, *s*- and *as*-diphenylurea, acenaphthenequinone (orange), 9 : 10-dinitroanthracene (yellow), benzanilide.

(3) In the following instances the glow was similar to the usual fluorescence spectrum: Anthracene, 1 : 2-benzanthracene, 9-phenylanthracene, 9 : 10-dichloro- and -dibromo-anthracenes, carbazole, aniline, α- and β-naphthylamines, diphenylamine, *p*-phenylenediamine. Probably also the blue glow given by a number of substances in the previous list is a continuation of the ultra-violet

fluorescence reaching up into the visible region under strong stimulation.

(4) Of those substances which gave banded spectra, only a minority have been completely investigated by photography. In other instances, the spectrum was too weak. Characteristic of all the stronger spectra was a well-marked head making an abrupt termination to the end of shorter wave-length. This head was often in the green region and never below the greenish-blue, but was sometimes in the red. The bands appeared on a bright continuous background, and to the blue side of the first head there was often a continuous spectrum also, although distinctly weaker.

The substances which have been photographed were chiefly aromatic hydrocarbons and naphthalene derivatives. Some of these have already been fully examined by Fischer, but others are now dealt with.

Toluene gave a continuous spectrum throughout the visible, but strongest between 4200 and 4800 Å. There was a strong band at $1/\lambda$ 2090, and others at 2193, 2151, and 1816.

p-*Cymene* glowed green and showed two distinct bands at $1/\lambda$ 2153 and 2083, and faint ones at 2222 and 1942, thus giving a series having an interval of about 70.

m-*Xylene* gave a spectrum less intense and much more diffuse than those of its isomerides (Fischer, *loc. cit.*). The same is true also of the absorption and fluorescence spectra. It showed, however, one very definite head at about $1/\lambda$ 2105 and signs of a second at 2224.

Mesitylene had five or six bands beginning in the bluish-green region, but fading quickly; it was not successfully photographed.

Naphthalene. The spectrum was in substantial agreement with Fischer's figures, but the first band on commencing excitation showed a doubling, which, however, was lost after a short time. The two heads were at $1/\lambda$ 1854 and 1850.

Tetrahydronaphthalene possessed a remarkably strong luminescence. Edge of spectrum, $1/\lambda$ 2123. Very strong double band, 2096 and 2075; also bands at about 2018, 1976, 1925, 1862, 1805, and 1715. The band 1925 is strong; the others are rather diffuse.

Octahydroanthracene also gave an intense spectrum starting at 2044 and having a strong double band at $1/\lambda$ 2043 and 2027. There were diffuse bands at about 1907, 1862, 1740, and a continuous region to the limit of the visible red.

Acenaphthene glowed orange-red and gave a number of bands which were fairly sharp on the blue edge in the case of the stronger ones. Positions, $1/\lambda$ 1767, 1748, 1717, 1691, 1629—1605, 1558. The fourth and the last are the strongest.

Triphenylmethane had a head at $1/\lambda$ 1930—1912 at the beginning of a continuous region extending to the limit of the red, with another diffuse maximum about 1750.

Diphenylmethane gave a yellowish-green glow which, however, was difficult to photograph. A change appeared to take place, the material giving a white solid of higher melting point.

α-*Methylnaphthalene* gave three strong bands, $1/\lambda$ 1825, 1690, 1556, and a faint one about 1640. There was also a strong continuous emission from the violet to 5000 Å.

β-*Methylnaphthalene* showed two strong heads, $1/\lambda$ 1657 and 1521, the former being particularly intense. There appeared to be a number of lesser maxima about 1815, 1780, 1604, and 1568, as well as a continuous region from the violet to 5000 Å.

α-*Naphthol* glowed red but soon fatigued, and showed only very indefinite maxima at about $1/\lambda$ 1664 and 1567.

β-*Naphthol* glowed less strongly than the last and more yellow in colour. The methyl ether showed bands at $1/\lambda$ 1757 and 1658.

Other substances which gave banded spectra were hexaethylbenzene, styrene, fluorene, phenylfluorene, chlorobenzene, *p*-dichlorobenzene, α-chloronaphthalene, hexachlorobenzene, ψ-cuminol, diphenylcarbinol, quinol dimethyl ether, anthraquinone, phenanthraquinone, *p*-tolyl methyl ether, 1 : 5-dihydroxynaphthalene, and α-naphthyl methyl ether.

Discussion of Results.

On comparing the anticathodic luminescence spectra with the Tesla-luminescence, it is apparent that what has been noted and described as the Tesla green glow (Marsh, *Phil. Mag.*, 1925, **49**, 971), from its usual appearance in a number of vapours, is substantially identical with the anticathodic glow of the solids, although there may be a strong anticathodic glow and yet little sign of emission from the vapour, *e.g.*, in naphthalene. In the cooled solids, the glow usually extends further towards the red than was found with the Tesla glow, and is stronger; and, as would be expected, the bands are displaced a little towards the region of greater wavelengths. This shift amounts to $1/\lambda$ 40 or more.

The position of the abrupt blue end of the anticathodic glow varies in a manner parallel with the variation of the absorption and fluorescence regions of the substance. There is a fairly definite frequency interval between the fluorescence and anticathodic glow regions. This is seen in the accompanying table, and must indicate a more or less fixed energy difference between two levels of activation common to all the substances.

TABLE I.

Substance.	Absorption-fluorescence boundary.	Anticathodic luminescence (short λ end).	Difference.
Toluene	3749	2151	1598
o-Xylene	3731	2099	1632
m-Xylene	3759	2108	1651
p-Xylene	3741	2131	1610
p-Cymene	3690	2153	1537
Tetrahydronaphthalene	3678	2085	1593
Octahydroanthracene	3528	2035	1493
Naphthalene	3245	1840	1405
Acenaphthene	3264	1767	1497
α-Methylnaphthalene	3333	1825	1508
β-Methylnaphthalene	3333	1815	1518
Triphenylmethane	3546	1921	1625
Styrene	3475	1912	1563

With the exception of naphthalene, the differences found do not vary by more than 10%.

The atomic-group spectra found in the infra-red show bands to a large extent independent of the exact molecular structure from which they originate, and although absorption bands of this series have been traced as far down as 0·606μ, they seem to have no direct connexion with the anticathodic bands. The above-noted interval between absorption or fluorescence and the anticathodic spectra, on the other hand, tends to show that the origin of the last is similar to that of the first two. Moreover, between the absorption, fluorescence, and anticathodic luminescence there is a distinctly traceable resemblance in structural detail. The clearest example of this is in *p*-xylene. Mies (*Z. wiss. Phot.*, 1909, **7**, 357) has measured 16 absorption bands divisible into two series giving an average interval $1/\lambda$ 79·5, and the anticathodic luminescence (Fischer) shows ten bands in two series with an average interval of 81·2. The Tesla-luminescence bands are again divisible into two series with an average interval of 81.

It must be admitted that not all the anticathodic luminescence spectra examined show a degree of regularity approaching that of *p*-xylene, but in most instances some sort of order is apparent in the case of the stronger heads, which, however, are often so diffuse that the accuracy of measurement scarcely justifies much deduction. In the case of naphthalene the three strongest bands appear at $1/\lambda$ 1840, 1694, and 1542, giving intervals of 146 and 152, similar in size to those found in other naphthalene spectra (Marsh, *Phil. Mag.*, 1925, **49**, 971; László, *Z. physikal. Chem.*, 1925, **118**, 369). The four strongest bands of acenaphthene (1558, 1617, 1691, and 1748) show intervals of 133 and 131. α- and β-Methylnaphthalenes give spectra resembling that of the parent hydrocarbon, but more

diffuse and having an average interval of about 135. The bands in the case of the β-derivative have undergone a shift towards the red region. In *p*-cymene, there is a regularity at intervals of 70 units, and so on. For a discussion of the significance of these intervals reference may be made to previous papers by the author (*Phil. Mag.*, 1925, **49**, 1206; J., 1926, 724).

Fischer found three equally-spaced broad bands between 4100 and 4700 Å. in very many of the substances he examined. Like several other workers, he has not recognised these as due to traces of anthracene. They belong to the ordinary fluorescence spectrum of this substance. On bombarding anthracene itself, they are produced, but not with particularly great intensity, and decomposition is rather rapid, but a mere trace of anthracene in another substance will give rise to them. The chemicals in which Fischer found these bands now ascribed to anthracene were: Naphthalene, β-naphthonitrile, α- and β-acetonaphthalide, α- and β-naphthol, α- and β-naphthylamine, dibenzyl, and phenanthrene.

It is worthy of note that benzaldehyde was found not to give an anticathodic glow. Most substances capable of light emission will give a fluorescence, a Tesla-luminescence, and an anticathodic glow. The Tesla glow of benzaldehyde, however, appears to be the only emission of which it is capable. This glow seems to bear some relation to the fluorescence, inasmuch as it occurs in the same position as the extra absorption band developed in concentrated sulphuric acid solutions, which, according to Baly, usually occurs in the fluorescence zone of the alcoholic solutions.

THE SIR DONALD CURRIE LABORATORIES, THE QUEEN'S UNIVERSITY, BELFAST, NORTHERN IRELAND. [*Received, June 28th*, 1926.]

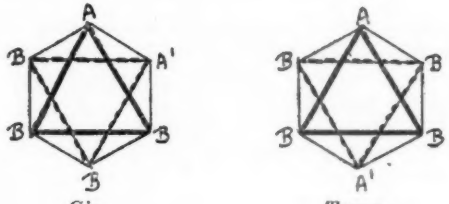
XXII.—*The Isomerism of Molybdenyl Monochloride.*

By WILLIAM WARDLAW and ROBERT LOUIS WORMELL.

THE results of conductivity measurements have shown that a wide range of chemical compounds has a co-ordination number of six. In the cases of cobalt, iron, chromium, rhodium, and iridium, of which the derivatives exhibit geometrical isomerism and are capable of resolution into optically active components, it has been proved that the six associating units have an octahedral distribution round the central metallic atom.

Determinations of the ionisation of a number of compounds of tervalent molybdenum have indicated a co-ordination number of six, but so far there is no evidence as to the spatial distribution of

the associating units. Three arrangements must be considered—the hexagon, the triangular prism, and the regular octahedron. Either of the first two configurations demands three isomeric forms for the complex [MAA'B_4], but if the units are situated at the vertices of a regular octahedron then only two stereoisomerides are possible, *viz.*, *cis-* and *trans-* :



Cis-. *Trans-*.

This important test has been applied to the co-ordination compound [MoOCl,4H_2O], and two isomeric forms have been isolated to which *cis-* and *trans*-configurations have been assigned. This has furnished the first indication that molybdenum can give rise to co-ordination compounds in accordance with Werner's view of their sixfold structure.

Experimental.

Brown Molybdenyl Monochloride.—In a previous communication (J., 1924, **125**, 2370), it was shown that when a solution of molybdenum trioxide in hydrochloric acid is reduced electrolytically to the tervalent condition, concentrated to small bulk, re-electrolysed, and the resulting reddish-brown liquid poured into air-free acetone, a buff-coloured solid separates, the analysis of which corresponds to MoOCl with approximately 4H_2O. It was later found that, on precipitating the oxychloride from a solution with a molybdenum content only one-fourth of that indicated in our paper (*loc. cit.*), the dried product gave an analysis in close accordance with that demanded by MoOCl,4H_2O (Found: Mo, 44·1; Cl, 16·3; Mo : Cl = 1 : 1. MoOCl,4H_2O requires Mo, 43·7; Cl, 16·2%).

Molecular-weight Determinations.—The molecular weight was determined by the depression of the freezing point of air-free water :

G. of MoOCl,4H_2O per 10 g. of water	0·2531	0·1669	0·1682
" Apparent " mol. wt.	191·3	185·6	186·1

The molecular weight for the non-ionised substance [MoOCl,4H_2O] is 219·5. Here, as in the case of many co-ordination compounds, the substance has apparently undergone hydrolysis whereby the

$$[MoOCl,4H_2O] + H_2O = [MoO,5H_2O]Cl = [MoO,5H_2O]^{\cdot} + Cl'.$$

co-ordinated chlorine atom is replaced by a molecule of solvent; this hydrolysis produces a binary electrolyte, the existence of which would influence the molecular-weight determinations in the foregoing manner. This progressive hydrolysis is also shown by the results of conductivity measurements at 1°.

For $v = 4$ litres per mole:

μ	33·7	38·1	39·9	40·8	44·8	46·8	50·8
Time (mins.) ...	4	8	12	15	43	80	220

For $v = 25$ litres per mole:

μ	33·0	38·9	42·9	45·7	48·2	49·7	51·1	52·3	53·3	65·2
Time (mins.)	2	3	4	5	6	7	8	9	10	40

In more dilute solutions, the rate of hydrolysis increased.

Now, for a binary electrolyte, *e.g.*, potassium chloride, the data at 1° are:

v (litres per mole)	8	16	32
μ	72·2	75·2	77·3

and the fact that the above conductivities alter with time and approach the value for a binary electrolyte, combined with the molecular-weight determinations, indicates that the brown oxychloride is not a binary electrolyte and that it is correctly formulated as the co-ordination compound $[MoOCl,4H_2O]$.

On the assumption that the six associating units are octahedrally distributed round the molybdenum atom, two isomeric oxychlorides should exist corresponding to *cis*- and *trans*-isomerism. The existence of this second molybdenyl chloride seems to be indicated from the fact that a solution of tervalent molybdenum in hydrochloric acid may be either reddish-brown or green, depending on the acid concentration. Chilesotti (*Z. Elektrochem.*, 1906, **12**, 146, 173) prepared the former solution by electrolytic reduction of molybdenum trioxide dissolved in 9N-hydrochloric acid, and the green solution was obtained when the acid used was 4—2·7N. Whilst the red solutions, having a content of 3·67% of molybdenum trioxide in the original solution and after complete reduction to the Mo^{III} stage, never exceed a static potential of $E_h = +0{\cdot}12$ volt at 24—26°, and are stable even in air, the green solutions under similar conditions attain potentials of $-0{\cdot}18$ volt and are readily oxidised by air and water—especially in contact with platinum—with evolution of hydrogen. A further difference between the two solutions was found by Bredig and Michel (*Z. physikal. Chem.*, 1922, **100**, 136), *viz.*, that the green solution reduces perchloric acid 2000 times as

quickly as the red. It was anticipated, therefore, that a green molybdenyl chloride would be isolated from the green solution of tervalent molybdenum and that it would be characterised by much greater reactivity than its brown isomeride. Such an oxychloride was obtained as follows.

Green Molybdenyl Monochloride.—A solution of molybdenum trioxide (60 g.) in 390 c.c. of hydrochloric acid (*d* 1·16) was diluted to 500 c.c., electrolysed for 4 hours in a diaphragm cell and concentrated at 50° under diminished pressure to 250 c.c. This concentrated solution, in which the molybdenum was quinquevalent, was then re-electrolysed. On prolonged electrolysis, the solution became green and the concentration of "free" acid diminished. At this stage, a portion of the solution, on being poured into acetone, gave a bluish-green precipitate, a typical hydrolysed product. The cell was now cooled in ice, and the cathode liquid forced by pressure of carbon dioxide into an equal volume of ice-cold 10*N*-hydrochloric acid. The olive-green solution thus produced was poured into air-free acetone and a green solid then separated in excellent yield. It was filtered off, washed with acetone, and dried in a vacuum desiccator. All these operations were performed in an atmosphere of carbon dioxide, air being rigidly excluded.

The valency of the molybdenum in this compound was determined as in the case of the brown oxychloride, and was found to be three.

Analysis.—The molybdenum was precipitated as sulphide and ignited to trioxide (J., 1924, **125**, 1911). The chloride in the filtrate and washings was estimated as silver chloride (Found: Mo, 46·2, 45·8; Cl, 17·2, 17·0; Mo : Cl = 1 : 1·01, 1 : 1·01. $MoOCl,3H_2O$ requires Mo, 47·6; $MoOCl,4H_2O$ requires Mo, 43·7%). As the solid had been dried in an evacuated desiccator, it is probable that its normal composition is $MoOCl,4H_2O$. These results show a close resemblance to those recorded (J., 1924, **125**, 2370) for the brown oxychloride isolated under similar conditions.

Properties and Reactions of Green Molybdenyl Chloride.—The freshly-precipitated solid is green, but on drying it becomes greyish-green. On exposure to the air, it darkens in colour and hydrolyses. It is more readily soluble in water and in concentrated hydrochloric acid than its brown isomeride, but is insoluble in alcohol. It has similar reducing properties to the brown oxychloride, but is much more reactive.

Molecular-weight Determinations.—The molecular weight was determined by depression of the freezing point of air-free water:

G. of $MoOCl,4H_2O$ per 10 g. of water ...	0·9774	1·0146	0·2302
"Apparent" mol. wt.	191·4	196·5	161·7

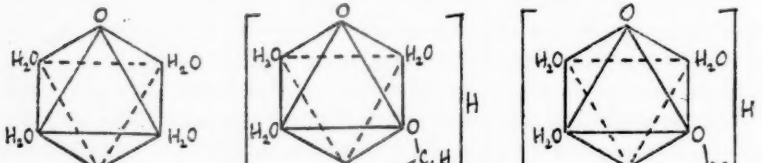
If the green solid were an ionisation isomeride of the brown oxychloride, it would be formulated as $[MoO]Cl,4H_2O$, in which case its apparent molecular weight would be 109·75 for complete ionisation. The above results indicate that green molybdenyl chloride should be formulated as $[MoOCl,4H_2O]$ and that it is much more rapidly hydrolysed than its isomeride. The results of conductivity measurements are open to the objection that during their determination the green solution undergoes slow oxidation by decomposition of the water, in the presence of the electrodes, with evolution of hydrogen. Nevertheless, in spite of the possibility of this side-reaction, the results obtained afford confirmatory evidence that the green solid has the co-ordination formula $[MoOCl,4H_2O]$:

At 1° for $v = 5·7$ litres per mole:

μ	42·77	48·9	50·6	51·9	53·1	53·6
Time (mins.)	1	3	4	5	6	7

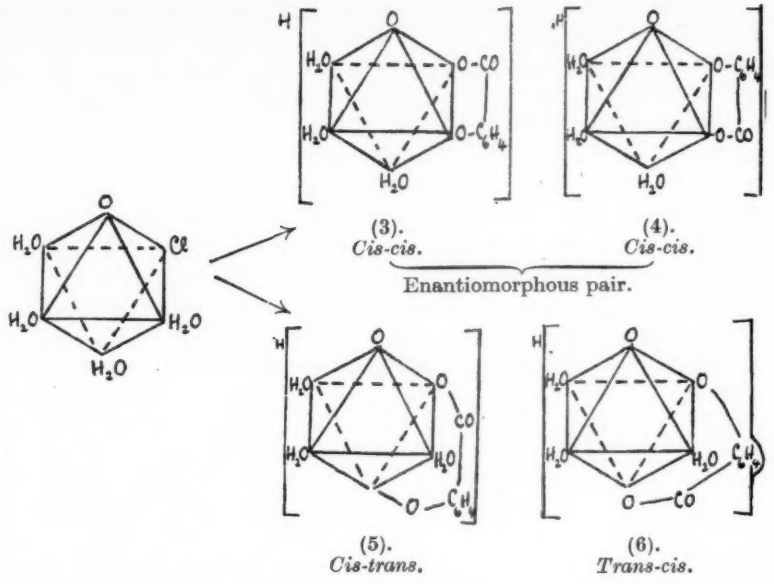
On the other hand, with concentrated solutions such as $v = 0·5$ litre per mole, the value of μ after one hour was only 19·7. These and other determinations indicated that by continuous hydrolysis a binary electrolyte was being formed, but that initially the compound was a non-electrolyte.

The Stereoisomerism of the Oxychlorides.—The existence of two isomeric co-ordination compounds, $MoOCl,4H_2O$, having been established, it is necessary now to assign to them *cis*- and *trans*-configurations. This has been made possible by a study of reactions in which the salicylate group has functioned as an unsymmetrical chelate group. Theoretical considerations indicate that by the interaction of monosodium salicylate, $NaH[O·C_6H_4·CO_2]$, and the *trans*-molybdenyl chloride, two products may be produced:



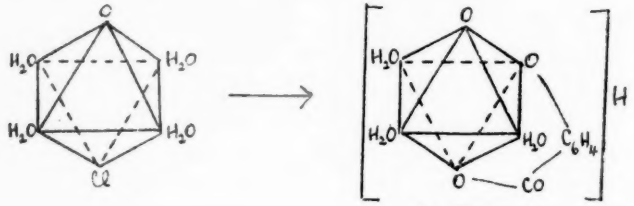
(1). *Trans-cis.* (2). *Cis-trans.*

By interaction of monosodium salicylate and *cis*-molybdenyl chloride, on the other hand, four products are theoretically possible, of which two (Nos. 3 and 4) are enantiomorphs:

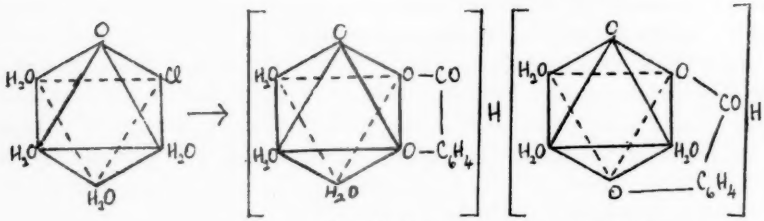


However, these different isomerides would be produced only on the assumption that the oxygen of the phenolic hydroxyl group and that of the carboxyl group equally well replace the chlorine unit in the co-ordination sphere. Experiment shows that this is not so. When the green oxychloride reacts with monosodium salicylate a precipitation of green molybdenyl salicylate takes place. This should theoretically be a mixture of isomerides (1) and (2). The interaction of the brown oxychloride and monosodium salicylate results in the formation of an insoluble brick-red substance, together with an intensely red-coloured liquid, which continuously deposits the insoluble product on keeping. Since (1) and (2) are identical with (5) and (6), it would be expected that the insoluble products from the green and brown oxychlorides would be identical, provided that products (1) and (2) as well as (5) and (6) were precipitated in equal proportions. The fact that these insoluble substances are clearly different in colour indicates a predominating replacement of the chlorine atom by either the carboxylic oxygen or the phenolic oxygen. To determine which was the more probable alternative, reactions were carried out with aqueous solutions of brown molybdenyl chloride and sodium phenoxide and sodium benzoate, respectively. In the case of the sodium phenoxide, molybdenum hydroxide was precipitated, whereas with the benzoate a well-characterised, insoluble derivative was obtained whose analysis corresponds to molybdenyl benzoate. These results indicate that

in the case of reactions with sodium salicylate and compounds of tervalent molybdenum the carboxylic oxygen replaces the co-ordinated chlorine atom and that the reaction itself is dependent on the presence of the carboxyl group. Whether this conclusion be accepted or not, there is no doubt, from the nature of the colours of the products, that the chlorine atom is replaced almost exclusively by either the phenolic or the carboxylic oxygen, and so the proof of *cis-* and *trans*-isomerism reduces itself to demonstrating that one isomeride, the *trans-*, should yield one product by reaction with monosodium salicylate, and that the other isomeride, the *cis-*, should give rise to two products, neither identical with the foregoing. On the assumption that the carboxylic oxygen replaces the chlorine atom, the following scheme will obtain :



(a) *Trans-cis.*



(b) *Cis-cis.* (c) *Cis-trans.*

By reaction of the green molybdenyl chloride and monosodium salicylate, one insoluble green molybdenyl salicylate has been obtained, the configuration of which must be in accordance with (a). From the brown molybdenyl chloride there is evidence of one soluble isomeride (b) and one brick-red insoluble isomeride (c), which is actually distinct from (a), as anticipated on theoretical grounds. A *cis*-configuration has therefore been assigned to the brown oxychloride, and a *trans-* to the green oxychloride.

Reaction between Monosodium Salicylate and Brown Molybdenyl Chloride.—Equimolecular aqueous solutions of monosodium salicylate and molybdenyl chloride were mixed together. With highly concentrated solutions, a brick-red molybdenyl salicylate separated in a few minutes and an intensely red supernatant liquid was produced. From more dilute solutions, the solid was precipitated

only after a longer period. In every case, however, the supernatant liquid was intensely red. On keeping, the red liquid continuously deposited the insoluble product, a process which was accelerated by warming. Undoubtedly two salicylates had been produced. One was insoluble in water whilst the other was readily soluble, producing a red solution. By intramolecular changes the soluble product was continuously changing to the insoluble isomeride.

Insoluble Molybdenyl Salicylate.—This solid was obtained as above, and, after filtration and washing free from the red, supernatant liquid by means of air-free water, it was dried in a desiccator over calcium chloride. The behaviour of the compound during the drying process is noteworthy. When the brick-red solid is dried out of contact with air, it darkens and ultimately yields the brown compound $[MoO{\cdot}O{\cdot}C_6H_4{\cdot}CO{\cdot}O,2H_2O]H$. It is impossible to isolate the brick-red substance in a dry condition because of these changes, but it seems reasonable to assume that they are associated with a decreasing content of water. The brown solid is practically insoluble in water, but when freshly prepared it is soluble in alcohol and in acetone.

The acidic nature of the compound is indicated by its ready solubility in ammonia and in dilute solutions of sodium or potassium hydroxide. After a time, the solid loses its ability to dissolve in organic solvents and becomes less soluble in ammonia.

Analysis.—The molybdenum was determined both by ignition of the compound to molybdenum trioxide and by precipitation as sulphide and ignition to the trioxide. Combustion of the solid gave water derived from both the hydrogen and the water of constitution (Found : Mo, 33·45; C, 29·2; H_2O, 28·3.

$[MoO{\cdot}O{\cdot}C_6H_4{\cdot}CO{\cdot}O,2H_2O]H$

requires Mo, 33·7; C, 29·5; $4{\cdot}5H_2O$ [from 9H], 28·4%). Analyses of other samples have indicated that the water content may vary between 2—$2{\cdot}5H_2O$.

Soluble Molybdenyl Salicylate.—Numerous attempts have been made to isolate a solid substance from the red, supernatant liquid formed in the interaction of the brown chloride and the sodium salicylate. Concentration of the liquid resulted in the formation of large quantities of the brown, insoluble isomeride, and the use of organic liquids neither precipitated nor extracted any product. The addition of pyridine, however, caused an immediate precipitation of a reddish-brown substance which, after washing and drying, proved to have the formula $\begin{matrix} C_5H_5N \\ MoO \end{matrix}\left[\begin{matrix} MoO{\cdot}O{\cdot}OC{\cdot}C_6H_4{\cdot}O \\ 3H_2O \end{matrix}\right]_2 H_2O$, which requires Mo, 35·4; C, 28·0; N, 1·7; $14H_2O$ (from 28H), 31·0 (Found : Mo, 35·2; C, 28·3; N, 1·6; H_2O, 30·0%).

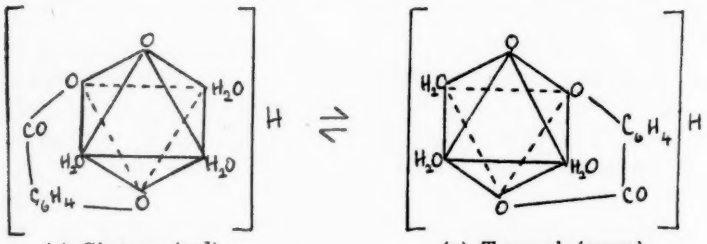
The isolation of this substance indicates the existence of the following equilibrium in the solution :

$$2[MoO{\cdot}O{\cdot}C_6H_4{\cdot}CO{\cdot}O]H \rightleftharpoons MoO[MoO{\cdot}O{\cdot}C_6H_4{\cdot}CO{\cdot}O] + OH{\cdot}C_6H_4{\cdot}CO_2H.$$

The addition of the pyridine disturbs the reaction in such a way as to form an increasing amount of $MoO[MoO{\cdot}O{\cdot}C_6H_4{\cdot}CO{\cdot}O]$, which is precipitated simultaneously with the pyridine salt of the soluble molybdenyl salicylate. Thus, although the molybdenyl salicylate has not been isolated, the results of the reaction with pyridine are strong evidence in favour of its existence and of its acidic character.

Reaction between Monosodium Salicylate and Green Molybdenyl Chloride.—On mixing an aqueous solution of sodium salicylate with a freshly-prepared, aqueous solution of green molybdenyl chloride, air being rigidly excluded, a pale green product was precipitated whilst the supernatant liquor was nearly colourless. The solid was separated and dried; a colour change from pale green to brown resulted, and the final product was almost identical in colour and properties with the dried insoluble molybdenyl salicylate prepared from the brown isomeric oxychloride. Analysis showed that the water content of the solid varied from $2—2{\cdot}5H_2O$ (Found : Mo, 32·4; C, 28·2; H_2O, 29·55. $[O{\cdot}C_6H_4{\cdot}CO{\cdot}O{\cdot}MoO,2{\cdot}5H_2O]H$ requires Mo, 32·65; C, 28·6; $5H_2O$ [from 10H], 30·6%).

A point of interest in connexion with the oxychlorides is that both the insoluble green molybdenyl salicylate and the insoluble brick-red isomeride give the same brown product on drying. Two explanations may be suggested. (1) This change of colour might be due to an intramolecular reaction whereby the same mixture of the isomerides (a) and (c) would result in both cases; there is the possibility that a brown product would result from a mixture of red and green substances. (2) An alternative view is that, by the loss



(c) *Cis-trans* (red). (a) *Trans-cis* (green).

of one molecule of water, the oxygen can occupy two positions in the co-ordination sphere—the analysis of the brown product indicates a water-content of $2—2{\cdot}5H_2O$—and it can readily be shown that by such a rearrangement the structures (c) and (a) become identical.

This question of the co-ordination number of oxygen will be dealt with in a later communication.

The authors desire to thank Messrs. Brunner Mond and Co., Ltd., and the Chemical Society for grants in aid of this investigation. One of them (R. L. W.) gratefully acknowledges receipt of a grant from the Department of Scientific and Industrial Research for part of the time during which this work was in progress.

UNIVERSITY OF BIRMINGHAM,
EDGBASTON. [*Received, October 16th*, 1926.]

XXIII.—*The Parachor and Chemical Constitution. Part IV. Three-membered and Four-membered Rings.*

By SAMUEL SUGDEN and HENRY WILKINS.

(1) *Three-membered Rings.*

IN the first paper on the parachor (Sugden, J., 1924, **125**, 1180), a provisional value of 22·3 was assigned to the constant for a three-membered ring. This was based upon a misconception of the structure of the nitro-group which has since been cleared up by the discovery of the effect of semipolar double bonds upon the molecular parachor (Sugden, Reed, and Wilkins, J., 1925, **127**, 1525). From the data there discussed it appears probable that the nitro-group has the structure $-N\begin{matrix}O\\ \diagdown\\ \diagup\\ O\end{matrix}$ and does not contain a three-membered ring.

In the present paper, data are given for nine substances which, from chemical evidence, undoubtedly possess a cyclic structure and from which the constant for a three-membered ring can be deduced.

The observed values of the parachors for these substances are in the second column of Table I; the column headed $\Sigma[P]$ gives the sum of the atomic and structural constants, except that for the three-membered ring, so that the effect of this structure is obtained by subtracting $\Sigma[P]$ from $[P]$ obs.

The mean value for the effect of the three-membered ring on the molecular parachor may be taken as 17, which is in good agreement with the figure predicted from the degree of unsaturation in such structures, as discussed later (Section 3). Individual substances give figures diverging by 3—4 units from this mean and such variations require consideration.

In the first place, these differences are much larger than the experimental errors of measurement. The estimated error in the density determinations is 0·1% and in the surface tensions 0·5%; if

TABLE I.

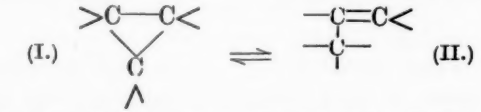
Parachor of Three-membered Rings.

Substance.	[P] obs.	Σ[P].	Structural constant.	Error of measurement.
1. Ethylene oxide	112·5	98·0	14·5	0·2
2. Epichlorohydrin	193·7	174·2	19·5	0·4
3. Ethyl *cyclo*propane-1 : 1-dicarboxylate	417·1	402·6	14·5	0·8
4. Ethyl *cyclo*propane-1 : 2-dicarboxylate	422·8	„	20·2	0·8
5. Ethyl *cyclo*propane-1 : 1 : 2 : 2-tetracarboxylate	701·1	688·2	12·9	1·4
6. Ethyl caronate	493·2	479·6	13·6	1·0
Esters of 3-methyl-Δ^2-*cyclo*propene-1 : 2-dicarboxylic acid.				
7. *normal* Methyl ester	371·6	352·6	19·0	0·8
8. „ Ethyl „	450·2	430·6	19·5	0·9
9. *labile* „ „	447·8	430·6	17·2	0·9
		Mean	16·7	

both errors are in the same direction, then (since the fourth root of the surface tension is used) the parachor is uncertain to 0·2% at most. The possible error thus introduced in the determination of the constant for the three-membered ring is given in the last column of Table I; it will be seen that it is much smaller than the differences found in the structural constant.

Further, it does not seem possible to account for these differences by the presence of impurities in some of the substances examined. Nos. 5, 7, and 8 are solids at the ordinary temperature and were recrystallised to constant melting point, whilst Nos. 3 and 4 were esters prepared from recrystallised acids of sharp melting point and boiled within 1°. Of the remaining liquids, epichlorohydrin was available in considerable quantity and was repeatedly dried and fractionated without producing any change in the surface tension or density, and the values found for the latter are in good agreement with those given by previous observers. The figure for ethylene oxide is calculated from the observations of Maass and Boomer (*J. Amer. Chem. Soc.*, 1922, **44**, 1709) on a carefully purified specimen. The esters 4 and 9 were purified by fractional distillation only; they boiled within 1°, and the parachors found for them fall well within the limits of the variation of the constant for a three-membered ring, so that there is no reason to suppose that they are seriously in error.

Another possible explanation of these differences is that some of the substances examined exhibit tautomerism and are mixtures of



isomerides having the structures (I) and (II). If this were the case,

the structural constant would approach that for a non-polar double bond (23·2) as the proportion of (II) increased. This explanation is excluded, however, for the substances having the structure (II) are in many cases well known and have different properties. Thus the esters 4, 5, and 6 are isomerides of, but not identical with, certain esters of the glutaconic series which have been well characterised.

It is obvious, therefore, that in this series, as in others (compare Sugden and Whittaker, J., 1925, **127**, 1868), the parachor is not strictly an additive function of atomic and structural constants, but that these constants vary slightly from substance to substance. The variation in the constant for the three-membered ring is in harmony with modern views as to the effect of substituents on the stability of rings; in particular, it is interesting to note that the lowest values, corresponding to a lower degree of unsaturation, are given by unsubstituted rings or by those containing a *gem*-group (compare Ingold, J., 1921, **119**, 305).

The figures for the esters of 3-methyl-Δ^2-*cyclo*propene-1 : 2-dicarboxylic acid are of special interest in view of the peculiar type of isomerism exhibited by the derivatives of this acid (Goss, Ingold, and Thorpe, J., 1923, **123**, 327, 3342; 1925, **127**, 460). The parachors found for these substances show clearly that both the normal and labile esters contain a three-membered ring and a non-polar double bond; if the isomerism were due to the presence of a semipolar double bond in either the labile or the normal form, the parachor would have been 25 units lower. This explanation of the remarkable type of isomerism exhibited by these compounds would be compatible with the fact that both forms have been obtained optically active, but is definitely excluded by the data quoted in Table I.

(2) *Four-membered Rings.*

In a previous paper (Sugden, *loc. cit.*), the value 12·0 was allotted to the effect on the parachor on a four-membered ring; this figure was based on observations of the surface tensions of limonene and pinene by Mitchell and Smith (J., 1913, **103**, 489). We have now measured three derivatives of *cyclo*butane with the results shown in Table II. It will be seen that the new data give good confirmation

TABLE II.

	[*P*] obs.	Σ[*P*].	Four-membered ring.
Ethyl 1-cyano*cyclo*butane-1-carboxylate	360·4	348·8	11·6
Ethyl *cyclo*butane-1 : 1-dicarboxylate	454·1	441·6	12·5
Ethyl *cyclo*butanecarboxylate	309·4	298·8	10·6
		Mean	11·6

of the older value and are also in good agreement with the constant calculated from the degree of unsaturation (see Section 3).

These *cyclo*butane derivatives were prepared by the method of Perkin and Carpenter (J., 1899, **75**, 921), and the esters measured were made *via* the silver salt from specimens of the free acids which had been carefully purified by crystallisation or distillation. The purification of the *cyclo*butane-1 : 1-dicarboxylic acid was effected by a specially devised method (see Experimental). The monocarboxylic ester prepared from this purified acid by the elimination of carbon dioxide and esterification boiled several degrees lower than Perkin and Carpenter's ester (*loc. cit.*), but its purity was confirmed by a determination of its saponification value.

(3) *Structural Constants and Unsaturation.*

It has been suggested in previous communications that the principal factor which determines the value of structural parachors is the intensity of unsaturation. This idea can now be expressed quantitatively, as all the more important constants are known with a fair degree of accuracy.

In Table III, col. 2 gives the number of latent valencies in the structure indicated in col. 1, or the number of hydrogen atoms required to convert each structure into an open-chain saturated compound. Col. 3 gives the number of octets which share this

TABLE III.

Structure.	Latent valencies (x).	Octets (n).	Degree of unsaturation (x/n).	Parachor. Obs.	Calc.
Triple bond	4	2	2·000	46·6	46·4
Double bond	2	2	1·000	(23·2)	(23·2)
Three-membered ring	2	3	0·667	17	15·5
Four-membered ring	2	4	0·500	11·6	11·6
Five-membered ring	2	5	0·400	8·5	9·3
Six-membered ring	2	6	0·333	6·1	7·7

unsaturation, whilst col. 4 gives the ratio x/n, which may be termed the degree of unsaturation. If it is assumed that the structural parachor is proportional to the degree of unsaturation, then, from the experimental value for the double bond (which is based upon the largest number of observations), the parachors for the other structures can be calculated. The numbers thus obtained are in col. 6, and they are seen to be in good agreement with the experimentally determined values in col. 5.

EXPERIMENTAL.

In the course of this work new measurements have been made of the surface tension and density of eleven compounds. The surface

tensions were determined by the method of maximum bubble pressure (Sugden, J., 1922, **121**, 858; 1924, **125**, 27); the constants for the bubblers used are :

Apparatus	4c.	4d.	5a.	8a.	9a.
r_2 (cm.)	0·139	0·139	0·140	0·206	0·216
A	0·004790	0·007767	0·006805	0·003712	0·00536

Densities were determined by the U-shaped pyknometer previously described (J., 1924, **125**, 1171) and are given in g./c.c. All temperatures recorded were obtained by comparison with a standard thermometer with *N.P.L.* certificate and are corrected for exposed stem.

The tables below are set out in the same manner as in previous papers and do not need further description. The parachor in the last column is calculated by the formula $[P] = \gamma^{1\cdot4}M/(D - d)$, where γ is the surface tension, M the molecular weight, D the density of the liquid, and d the density of the vapour.

Ethylene oxide, C_2H_4O; $M = 44·04$. The values of γ, D, and d are taken from the paper of Maass and Boomer (*loc. cit.*).

t.	γ(dynes/cm.).	$(D-d)$ (g./c.c.).	Parachor.
−52·0°	36·4	0·9657	112·0
−43·4	34·8	0·9545	112·1
−26·2	31·9	0·9316	112·4
−15·0	30·3	0·9164	112·7
− 5·0	28·4	0·9027	112·6
5·8	26·8	0·8879	112·9
13·3	25·4	0·8805	112·3
20·0	24·3	0·8679	112·7
		Mean	112·5

Epichlorohydrin, C_3H_5OCl, $M = 92·51$, was dried over calcium chloride and boiled at 115° (corr.)/740 mm. Densities determined : $D^{10°}_{4°}$ 1·190, $D^{33°}_{4°}$ 1·161, $D^{55°}_{4°}$ 1·136, $D^{71°}_{4°}$ 1·116, whence $D^{t°}_{4°} = 1·202 - 0·00119t$. These values are in good agreement with those of Thorpe (J., 1880, **37**, 207).

App.	t.	P.	D.	ϕ.*	γ.	Parachor.
9a	12·5	6939	1·187	1·0250	38·13	193·6
,,	31	6447	1·165	1·0264	35·48	193·7
,,	50·5	5964	1·142	1·0280	32·86	193·9
,,	68·5	5504	1·121	1·0298	30·38	193·7
,,	89	5011	1·096	1·0320	27·72	193·6
					Mean	193·7

* A correction factor, see J., 1924, **125**, 31.

Ethyl cyclo*propane*-1 : 1-*dicarboxylate*, $C_9H_{14}O_4$, $M = 186·2$, was prepared *via* the silver salt from purified acid which had been recrystallised from benzene until its melting point was constant. The ester boiled at 218° (corr.)/769 mm. Densities determined :

$D_4^{15°}$ 1·071, $D_4^{50°}$ 1·034, $D_4^{83°}$ 0·988, $D_4^{139°}$ 0·940, whence $D_4^{t°} = 1·087 - 0·00105t$.

App.	t.	P.	$D-d$.	ϕ.	γ.	Parachor.
4c	25	6430	1·061	1·0155	31·28	415·1
9a	75	4712	1·008	1·0313	26·05	417·4
4c	110	4633	0·971	1·0197	22·62	418·3
9a	134	3641	0·946	1·0380	20·25	417·6
4c	153	3780	0·925	1·0230	18·52	417·7
9a	164	3141	0·914	1·0425	17·55	417·1
4c	189	3156	0·887	1·0264	15·52	416·7
					Mean	417·1

Ethyl cyclo*propane*-1 : 2-*dicarboxylate*, $C_9H_{14}O_4$, $M = 186·2$, was twice distilled under diminished pressure; the specimen used boiled at 106·5—107·5° (corr.)/11 mm. Densities determined: $D_4^{13°}$ 1·062, $D_4^{54°}$ 1·020, $D_4^{81°}$ 0·993, whence $D_4^{t°} = 1·075 - 0·00101t$.

App.	t.	P.	D.	ϕ.	γ.	Parachor.
5a	11	4810	1·064	1·0210	33·41	420·9
8a	14	8802	1·061	1·0168	33·22	421·3
5a	54	4154	1·020	1·0233	28·92	423·4
8a	71	7215	1·003	1·0194	27·29	424·3
5a	90	3607	0·984	1·0258	25·17	423·9
					Mean	422·8

Ethyl cyclo*propane*-1 : 1 : 2 : 2-*tetracarboxylate*, $C_{15}H_{22}O_8$, $M = 330·2$, was recrystallised from ligroin and melted sharply at 43° (corr.). Densities determined: $D_4^{57°}$ 1·117, $D_4^{69°}$ 1·104, $D_4^{77°}$ 1·096, $D_4^{83·2°}$ 1·090, whence $D_4^{t°} = 1·176 - 0·00104t$.

App.	t.	P.	D.	ϕ.	γ.	Parachor.
5a	76	4170	1·097	1·0250	29·08	699·0
,,	97	3876	1·075	1·0264	27·08	700·8
,,	122	3537	1·049	1·0282	24·75	702·2
,,	152	3127	1·018	1·0308	21·93	702·2
					Mean	701·1

Ethyl caronate (*ethyl* trans-3 : 3-*dimethyl*cyclo*propane*-1 : 2-*dicarboxylate*), $C_{11}H_{18}O_4$, $M = 214·2$, was prepared from recrystallised caronic acid and absolute alcohol and boiled at 244° (corr.)/762 mm. Densities determined: $D_4^{11°}$ 1·035, $D_4^{30·5°}$ 1·015, $D_4^{53°}$ 0·992, $D_4^{71°}$ 0·973, whence $D_4^{t°} = 1·046 - 0·00103t$.

App.	t.	P.	D.	ϕ.	γ.	Parachor.
4d	12	3965	1·034	1·0245	31·56	491·0
,,	34	3662	1·011	1·0260	29·19	492·5
,,	54	3395	0·990	1·0275	27·10	493·7
,,	63·5	3258	0·981	1·0283	26·02	493·1
,,	75	3128	0·969	1·0291	25·00	494·3
,,	93·5	2890	0·950	1·0309	23·15	494·6
					Mean	493·2

normal *Methyl* 3-*methyl*-Δ^2-cyclo*propene*-1 : 2-*dicarboxylate*, $C_8H_{10}O_4$, $M = 170·1$. White crystals, m. p. 33—34° (corr.). Densities determined: $D_4^{39°}$ 1·123, $D_4^{57°}$ 1·103, $D_4^{71°}$ 1·087, $D_4^{91°}$ 1·064, whence $D_4^{t°} = 1·169 - 0·00115t$.

App.	*t.*	*P.*	*D.*	ϕ.	γ.	Parachor.
4d	42	4460	1·121	1·0237	35·46	370·3
,,	63	4138	1·097	1·0250	32·94	371·4
,,	81	3863	1·076	1·0262	30·79	372·4
,,	95	3632	1·060	1·0275	28·98	372·3
					Mean	371·6

normal *Ethyl* 3-*methyl*-Δ^2-cyclo*propene*-1 : 2-*dicarboxylate*, $C_{10}H_{14}O_4$, $M = 198{\cdot}1$. White crystals, m. p. 38—39° (corr.). Densities determined : $D_{4^\circ}^{14{\cdot}5^\circ}$ 1·038, $D_{4^\circ}^{20{\cdot}5^\circ}$ 1·024, $D_{4^\circ}^{31{\cdot}5^\circ}$ 1·001, whence $D_{4^\circ}^{t^\circ} = 1{\cdot}084 - 0{\cdot}00100t$.

App.	*t.*	*P.*	*D.*	ϕ.	γ.	Parachor.
4d	41·5	3947	1·042	1·0248	31·42	450·1
,,	51	3803	1·033	1·0255	30·33	450·1
,,	62	3653	1·022	1·0263	29·12	450·2
,,	77·5	3448	1·007	1·0275	27·52	450·6
					Mean	450·2

labile *Ethyl* 3-*methyl*-Δ^2-cyclo*propene*-1 : 2-*dicarboxylate*, $C_{10}H_{14}O_4$, $M = 198{\cdot}1$. This ester was prepared by distilling the normal ester at atmospheric pressure (compare Goss, Ingold, and Thorpe, *loc. cit.*). Considerable decomposition and gas evolution took place; the distillate fractionated under diminished pressure gave a 50% yield of an oil, b. p. 155—156° (corr.)/19 mm., which was regarded as the labile ester. Densities determined : $D_{4^\circ}^{23^\circ}$ 1·072, $D_{4^\circ}^{40{\cdot}5^\circ}$ 1·054, $D_{4^\circ}^{64{\cdot}5^\circ}$ 1·029, whence $D_{4^\circ}^{t^\circ} = 1{\cdot}096 - 0{\cdot}00103t$.

App.	*t.*	*P.*	*D.*	ϕ.	γ.	Parachor.
4d	26	4275	1·069	1·0235	33·98	447·5
,,	50	3911	1·045	1·0252	31·13	447·8
,,	77	3507	1·017	1·0273	27·99	448·0
					Mean	447·8

Ethyl 1-*cyano*cyclo*butane*-1-*carboxylate*, $C_8H_{11}O_2N$, $M = 153{\cdot}1$. The crude ester was prepared by the condensation of cyanoacetic ester and trimethylene bromide (Perkin and Carpenter, *loc. cit.*); the yield was low in the first runs, but was raised to 67% by using alcohol dried with the aluminium–mercury couple. The crude ester (b. p. 99—102°/14 mm.) was partly hydrolysed with a slight excess of methyl-alcoholic potash, and the free cyano-acid recrystallised twice from benzene; it then melted sharply at 67—68° (corr.). From this, the ethyl ester was prepared *via* the silver salt and boiled at 215·5—216° (corr.)/762 mm. Densities determined : $D_{4^\circ}^{13{\cdot}5^\circ}$ 1·045, $D_{4^\circ}^{42^\circ}$ 1·015, $D_{4^\circ}^{70{\cdot}5^\circ}$ 0·988, $D_{4^\circ}^{93^\circ}$ 0·966, whence $D_{4^\circ}^{t^\circ} = 1{\cdot}058 - 0{\cdot}000995t$.

App.	*t.*	*P.*	*D.*	ϕ.	γ.	Parachor.
4d	13·5	4495	1·045	1·0219	35·68	358·1
,,	46	4011	1·012	1·0237	31·88	359·5
,,	57	3887	1·001	1·0242	30·92	360·7
,,	69·5	3673	0·989	1·0253	29·26	360·1
,,	84·5	3495	0·974	1·0262	27·86	361·1
,,	111·5	3128	0·947	1·0285	24·99	361·5
,,	126·5	2936	0·932	1·0299	23·49	361·7
					Mean	360·4

Ethyl cyclo*butane*-1 : 1-*dicarboxylate*, $C_{10}H_{16}O_4$, $M = 200{\cdot}2$. The crude cyano-ester on complete hydrolysis gave a mixture of the required dibasic acid and malonic acid derived from unchanged cyanoacetic ester. This mixture was difficult to separate by crystallisation from any solvent, but the malonic acid was removed completely in the following manner. The mixed acids were dissolved in excess of 5% ammonia, and barium chloride solution was added until no further precipitate was produced. The precipitate of barium malonate was filtered off, and the filtrate, after acidification and extraction with ether, gave nearly pure *cyclo*butane-1 : 1-dicarboxylic acid, which, after one crystallisation from benzene, melted at 156·5° (corr.). From this, the ester was prepared *via* the silver salt; b. p. 228·5—229·5° (corr.)/755 mm. Densities determined: $D_4^{15\cdot5°}$ 1·054, $D_4^{31\cdot5°}$ 1·017, $D_4^{79°}$ 0·990, $D_4^{99°}$ 0·969, whence $D_4^{t°} = 1{\cdot}070 - 0{\cdot}00102t$.

App.	t.	P.	D.	ϕ.	γ.	Parachor.
4d	15	4086	1·054	1·0243	32·51	453·5
,,	49	3601	1·0195	1·0266	28·70	454·4
,,	81	3157	0·987	1·0294	25·24	454·5
					Mean	454·1

Ethyl cyclo*butanecarboxylate*, $C_7H_{12}O_2$, $M = 128{\cdot}1$. The pure dicarboxylic acid lost carbon dioxide smoothly at 185—190° and gave a good yield of the monobasic acid, b. p. 190—192° (corr.)/762 mm. The ethyl ester prepared *via* the silver salt was repeatedly fractionated and boiled at 152—154° (corr.)/756 mm. (Perkin and Carpenter give 159—162°). The purity of the ester was therefore checked by a determination of its equivalent by hydrolysis with potash (Found: 127·0. Calc.: 128·1). Densities determined: $D_4^{21°}$ 0·956, $D_4^{45\cdot5°}$ 0·941, $D_4^{70°}$ 0·927, $D_4^{\ddagger5°}$ 0·911, whence $D_4^{t°} = 0{\cdot}988 - 0{\cdot}00103t$.

App.	t.	P.	D.	ϕ.	γ.	Parachor.
4d	19·5	3766	0·968	1·0242	29·96	309·5
,,	47·5	3335	0·939	1·0265	26·58	309·6
,,	70	3016	0·916	1·0286	24·10	309·8
,,	90·5	2707	0·895	1·0311	21·68	308·8
					Mean	309·4

Summary.

1. The "structural" parachor for a three-membered ring is found to be 17; individual substances show variations of a few units from this value.

2. Both the normal and the labile forms of esters of 3-methyl-*cyclo*propenedicarboxylic acid contain a non-polar double bond.

3. The value for a four-membered ring is shown to be 11·6.

4. Structural parachors are proportional to the degree of unsaturation of the multiple bond or ring structure concerned.

The authors wish to express their thanks to Prof. C. K. Ingold, F.R.S., for the loan of substances 4, 5, 7, and 8 in Table I, and to Mr. R. G. Atkinson for a specimen of synthetic caronic acid. One of us (S. S.) is also indebted to the Research Fund Committee of this Society for a grant which has partly defrayed the cost of this investigation.

BIRKBECK COLLEGE (UNIVERSITY OF LONDON),
LONDON, E.C. 4. [*Received, November 6th*, 1926.]

XXIV.—*An Electrometric Study of Tungstic Acid.*

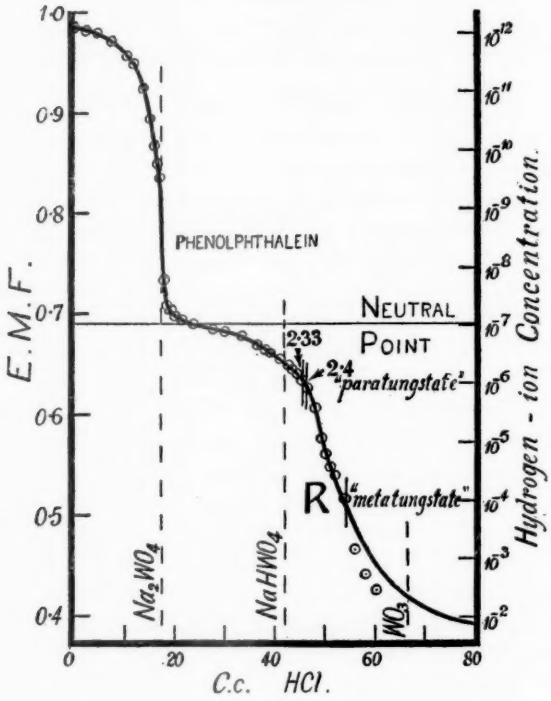
By HUBERT THOMAS STANLEY BRITTON.

THE facts that tungstic oxide forms salts with the alkali metals, R_2WO_4, and that tungsten appears in the same group of the periodic system as sulphur have led to the impression that tungstic acid is an ordinary dibasic acid. An attempt was made to study the acidic nature of the oxide by following electrometrically the variation in hydrogen-ion concentration during the course of its neutralisation with sodium hydroxide; for this purpose, however, it was found more convenient to back-titrate a solution of the oxide in sodium hydroxide with hydrochloric acid. The first portion of the titration curve, given in Fig. 1, was constructed from *E.M.F.* measurements at 20° made between a hydrogen electrode immersed in the solution and a normal calomel half-element, the junction liquid being a saturated solution of potassium chloride. The titration was performed as previously described (J., 1924, **125**, 1572) and the *P.D.*'s were found to be reproducible until 0·5 volt was reached ($[H^{\cdot}] = 10^{-4}$). At this stage, the hydrogen in the electrode began to reduce catalytically the sexavalent tungsten to the quinquevalent state, as indicated by the appearance of the characteristic blue coloration around the electrode. This position is denoted by R on the curve. The three points on the diagram obtained after reduction became obvious represent initial readings made before the effect of the reduction had become appreciable. To complete the titration curve, resort was made to the oxygen electrode, with which a similar titration was carried out using solutions of the same concentrations. Neither the hydrogen-electrode nor the oxygen-electrode curve showed that any abrupt changes in hydrogen-ion concentration occurred in solutions more acidic than p_H 4. The remaining portion of the curve in Fig. 1 was plotted from the oxygen-electrode curve, calibrated against the portion obtained with the hydrogen electrode, the accuracy of which

is considered to be of the order of one-tenth of a p_H unit (compare J., 1924, **125**, 1572; 1925, **127**, 1896). The curve given in Fig. 1 represents the titration by 0·1020*N*-hydrochloric acid of 100 c.c. of a solution which was 0·0678*N* with respect to sodium hydroxide and 0·0250*M* with respect to tungstic acid (WO_3).

The curve shows that a sharp diminution in p_H took place with the amount of hydrochloric acid necessary to react with the alkali in excess of that required to form the normal sodium tungstate.

FIG. 1.



This explains why tungstic acid may be estimated volumetrically either by titrating a suspension of it directly with sodium hydroxide or by dissolving the oxide in alkali and titrating the excess of alkali with acid, using in each case phenolphthalein as indicator (Hundeshagen, *Chem.-Ztg.*, 1894, **18**, 547; Herting, *Z. angew. Chem.*, 1901, **14**, 165; Lind and Trueblood, *J. Amer. Chem. Soc.*, 1907, **29**, 477). The remaining part of the curve down to the dotted line indicating WO_3 represents, in effect, the reverse of the neutralisation of tungstic acid with sodium hydroxide. The large inflexion produced when the acid was about one-quarter neutralised

is surprising in that it did not occur when the acid was half neutralised, as would have been the case had tungstic acid behaved as an ordinary dibasic acid with widely differing dissociation constants.

No precipitation of tungstic oxide occurred throughout the titration even although a large excess of hydrochloric acid had been added. The solution remained perfectly clear, suggesting that the oxide had passed into a sub-colloidal state and not into combination with the hydrochloric acid, which would have been indicated by the p_H readings. It is of course possible that the hydrochloric acid had some stabilising influence through being slightly adsorbed by or feebly combined with the tungstic oxide. Using more concentrated solutions, precipitation ensues (see van Liempt, *Z. anorg. Chem.*, 1923, **127**, 215; *Rec. trav. chim.*, 1924, **43**, 30).

The curve throws some light on the so-called " paratungstates " and " metatungstates." Sodium paratungstate is stated to have the composition $3Na_2O,7WO_3,21H_2O$ or $5Na_2O,12WO_3,28H_2O$, and thus it contains either 2·33 or 2·4 mols. of Na_2O to 1 mol. of WO_3. The points on the titration curve marked 2·33 and 2·4 indicate the hydrogen-ion concentrations of the solutions when the solutes were present in those ratios, the p_H being 6·1 and 6·0, respectively. Schmidt (*Amer. Chem. J.*, 1886, **8**, 16) found that a solution of the 2·4-salt was acidic to rosolic acid and alkaline to cochineal; consequently the p_H of his solution was in the neighbourhood of 6, and is thus in accord with the value indicated by the curve. The point marked " metatungstate " gives the hydrogen-ion concentration, 10^{-4}, of the solution when the alkali in combination with the tungstic acid was that required by $Na_2W_4O_{13}$, the formula for sodium metatungstate. Although the hydrogen-ion concentrations of the " para " and " meta " solutions show that some kind of union has taken place, it is difficult to picture the exact nature of that union. It appears from the curve that the paratungstate solution is the same as that of a solution of sodium tungstate saturated with tungstic oxide such that the change in hydrogen-ion concentration undergone is very small, whereas the metatungstate solution corresponds to a still greater saturation, but one which involves a considerable variation in hydrogen-ion concentration. These are the conditions which underlie the preparation of these salts. Seeing that tungstic acid cannot be considered as an ordinary dibasic acid, it is not apparent what kind of compounds these are, unless it be supposed that they contain tungstic acid either in a polymerised form or in a semi-colloidal form, which on dissolution in water gives rise to a micellar ionisation.

The author thanks the Department of Scientific and Industrial Research for a personal grant, the Chemical Society for a Research Grant, and Prof. Philip, F.R.S., for kindly placing facilities at his disposal.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7. [*Received, December 1st*, 1926.]

XXV.—*Complex Formation amongst the Nitrates. Part I. The Ternary System Copper Nitrate–Cobalt Nitrate–Water.*

By KATHLEEN WINIFRED WILCOX and CHARLES REYNOLDS BAILEY.

NITRATO-SALTS or double nitrates have not been investigated with thoroughness. The known examples are generally confined to cases where one metal is of high atomic weight and volume, *e.g.*, $3Ni(NO_3)_2,2Ce(NO_3)_3,24H_2O$ and $2KNO_3,Ba(NO_3)_2$, although some nitrato-acids are also known. It was noticed that a mixture of copper and cobalt nitrates set to a hard mass on keeping. This phenomenon has generally been held to indicate chemical or physical reaction, whilst Hedvall and Heuberger (*Z. anorg. Chem.*, 1924, **135**, 49) and Tammann (*ibid.*, 1925, **149**, 21) have measured the rate of reaction in powdered mixtures of crystals.

The Binary Systems.

(i) *Copper Nitrate–Water.*—The hydrates of copper nitrate have been extensively studied; the anhydrous nitrate has been prepared by Ditte (*Compt. rend.*, 1879, **89**, 576, 641) and by Guntz and Martin (*Bull. Soc. chim.*, 1909, **5**, 1004). Certain complexes are known containing anhydrous copper nitrate. Funk (*Z. anorg. Chem.*, 1899, **20**, 412), from a solubility curve, inferred the existence of a nona-, a hexa-, and a tri-hydrate, and these have been generally accepted although Richards (*Amer. Chem. J.*, 1898, **20**, 706, footnote) suggested that the formula of the so-called trihydrate should be $3Cu(NO_3)_2,8H_2O$. Schreinemakers, Berkhoff, and Posthumus (*Rec. trav. chim.*, 1924, **43**, 508) showed that the hydrate crystallising from ternary mixtures of copper nitrate, ammonium nitrate, and water has the composition $Cu(NO_3)_2,2\frac{1}{2}H_2O$. This is fully confirmed in the present work and in unpublished analyses by one of the authors of the ternary system copper nitrate–silver nitrate–water; in the first case the tie-lines intersect the copper nitrate–water side of the triangle at points corresponding to 80·9, 80·8, and 80·2% $Cu(NO_3)_2$ [Calc. for $Cu(NO_3)_2,2\frac{1}{2}H_2O$: 80·6; for

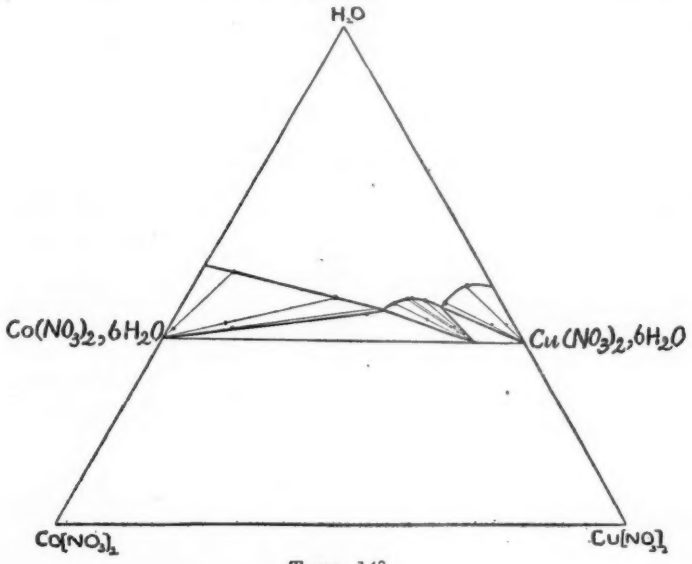
$3Cu(NO_3)_2,8H_2O$: 79·6%]. The crystals which Richards analysed were isolated from the binary system and kept over strong caustic potash solution : it is possible that they contained mother-liquor.

The solubility of copper nitrate in water at various temperatures is given in Table I as g. of $Cu(NO_3)_2$ per 100 g. of solution.

TABLE I.

Temp.	$Cu(NO_3)_2$ (%).	Hydrate present.	Temp.	$Cu(NO_3)_2$ (%).	Hydrate present.
15·0°	52·8	$6H_2O$.	30·0°	61·4	$2\frac{1}{2}H_2O$.
20·0	55·6	,,	35·0	62·0	,,
25·0	60·1	,,	40·0	62·6	,,
25·4	60·8	$6H_2O,2\frac{1}{2}H_2O$.			

FIG. 1.



Temp. 14°.

These results differ from those of Funk (*loc. cit.*), especially at the higher and lower temperatures. In addition, the temperature of the transition point is 25·4°, whereas Funk gives 24·5°—this is probably a misprint, as this point lies off his curve. Meijer (*Rec. trav. chim.*, 1924, **43**, 397), in examining the system copper nitrate–ammonium nitrate–water, obtained certain values for the solubility of copper nitrate in water, but as he failed to isolate the compound described by Schreinemakers, Berkhoff, and Posthumus (*loc. cit.*) from the same system, and as he did not question the existence of the trihydrate, it is not surprising that his solubility values depart largely from the above.

(ii) *Cobalt Nitrate–Water.*—Within the temperature limits of this investigation, this system does not call for detailed criticism: the solubilities as given by Funk (*Z. anorg. Chem.*, 1899, **20**, 412) seem to be consistently too high: the values now obtained are given in Table II, the solid phase throughout being $Co(NO_3)_2,6H_2O$.

TABLE II.

Temp.	15·0°	20·0°	25·0°	30·0°
$Co(NO_3)_2$ (%)	47·7	49·3	50·7	52·8

The Ternary System.

Three temperatures were chosen for investigation: 30°, just above the copper nitrate transition point; 20°, just below it; and 14°, at which a double salt was found to exist (see Fig. 1). This compound has the probable formula $6Cu(NO_3)_2,Co(NO_3)_2,42H_2O$,

TABLE III.

	Solution.		Residue.		
$d^{20°}_{20°}$.	% $Cu(NO_3)_2$.	% $Co(NO_3)_2$.	% $Cu(NO_3)_2$.	% $Co(NO_3)_2$.	Solid phase.
Temperature 14°.					
—	52·5	—	—	—	$Cu(NO_3)_2,6H_2O$.
—	47·0	5·9	60·2	1·5	,,
—	45·6	11·1	58·8	3·0	,,
—	41·5	14·0	52·8	9·4	Double salt.
—	38·9	16·0	50·2	10·8	,,
—	38·4	16·7	51·3	10·4	,,
—	36·5	19·0	47·4	12·6	,,
—	34·1	22·8	9·6	51·9	$Co(NO_3)_2,6H_2O$.
—	25·8	28·7	7·9	52·8	,,
—	5·2	44·3	1·5	59·0	,,
—	—	47·5	—	—	,,
Temperature 20°.					
—	55·6	—	—	—	$Cu(NO_3)_2,6H_2O$.
1·707	49·8	8·9	58·9	3·1	,,
—	49·4	10·8	57·8	4·9	,,
—	45·0	16·7	20·0	42·5	$Co(NO_3)_2,6H_2O$.
1·773	43·1	17·9	19·4	43·2	,,
1·705	33·7	24·5	14·8	46·7	,,
1·640	20·3	34·2	7·2	52·9	,,
1·613	13·1	38·9	3·4	56·8	,,
1·610	9·9	41·2	3·0	57·0	,,
1·598	—	49·3	—	—	,,
Temperature 30°.					
—	61·4	—	—	—	$Cu(NO_3)_2,2\frac{1}{2}H_2O$.
—	54·9	5·3	68·7	2·5	,,
—	48·4	13·0	75·9	1·9	,,
—	45·7	16·5	71·2	4·1	,,
—	37·9	22·2	9·8	52·4	$Co(NO_3)_2,6H_2O$.
—	27·1	29·2	5·6	55·5	,,
—	9·2	44·7	2·2	59·4	,,
—	—	52·7	—	—	,,

is very deliquescent, and melts at *ca.* 17°; as it is decomposed by water, its composition cannot be determined very accurately, the uncertainty corresponding to about $1H_2O$. The double salt is smoke-blue and crystallises from a magnificent purple solution.

The solutions and corresponding residues were examined in each case, and the data are in Table III.

Cobalt was determined by conversion of both metals to sulphate and electrolysis of the ammoniacal formate solution after removal of copper. Copper was determined by electrolysis of the nitric acid solution and also iodometrically: concordant results were obtained. A further check was made in the binary systems by determining both cobalt and copper as the anhydrous sulphates.

Summary.

1. The ternary system copper nitrate–cobalt nitrate–water has been examined at 14°, 20°, and 30°.

2. A complex has been isolated containing 6 mols. of the hexahydrate of copper nitrate to 1 mol. of the hexahydrate of cobalt nitrate, *i.e.*, $6Cu(NO_3)_2,Co(NO_3)_2,42H_2O$.

3. Copper nitrate "trihydrate" is shown to have the composition $Cu(NO_3)_2,2\frac{1}{2}H_2O$.

The authors tender their thanks to the Research Fund Committee of the Chemical Society for a grant which has covered the cost of the materials used.

THE SIR WILLIAM RAMSAY LABORATORIES OF PHYSICAL AND INORGANIC CHEMISTRY, UNIVERSITY COLLEGE, LONDON. [*Received, November 24th,* 1926.]

XXVI.—*The Movement of Flame in Closed Vessels: Correlation with Development of Pressure.*

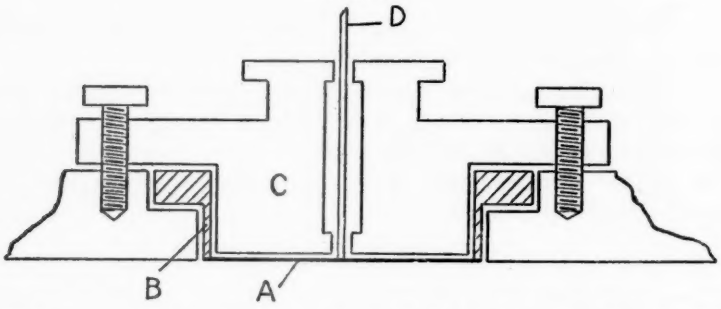
By OLIVER COLIGNY DE CHAMPFLEUR ELLIS and RICHARD VERNON WHEELER.

IT has been generally assumed in the past that, when a highly explosive mixture is ignited at the centre of a sphere, the moment of attainment of maximum pressure must synchronise with the moment of complete inflammation of the mixture, *i.e.*, with the moment at which the flame, the propagation of which follows regular concentric spherical surfaces, reaches the boundary of the vessel, which it does simultaneously at all points (see J., 1925, **127**, 764).

Langen ("Mitteilungen u. Forschungsarbeiten aus dem Gebeite des Ingenieurwesens," 1903, 8) seems to have been the first to

realise that, if this assumption be correct, the interpretation of time–pressure diagrams, and particularly of cooling-curves, obtained by means of a continuously recording pressure-gauge attached to the wall of the explosion-vessel, can best be made when the vessel is spherical and ignition central. His experiments, made mainly for the purpose of determining the specific heats of gases at high temperatures, were therefore carried out under such conditions, his explosion-vessel having a spherical cavity of 33·5 litres capacity. Regarding such work, Dugald Clerk ("The Gas, Petrol, and Oil Engine," Vol. 1, p. 136, London, 1910) stated that "all physicists who have experimented on the subject agree in considering that inflammation is complete * when the highest pressure is attained."

FIG. 1.

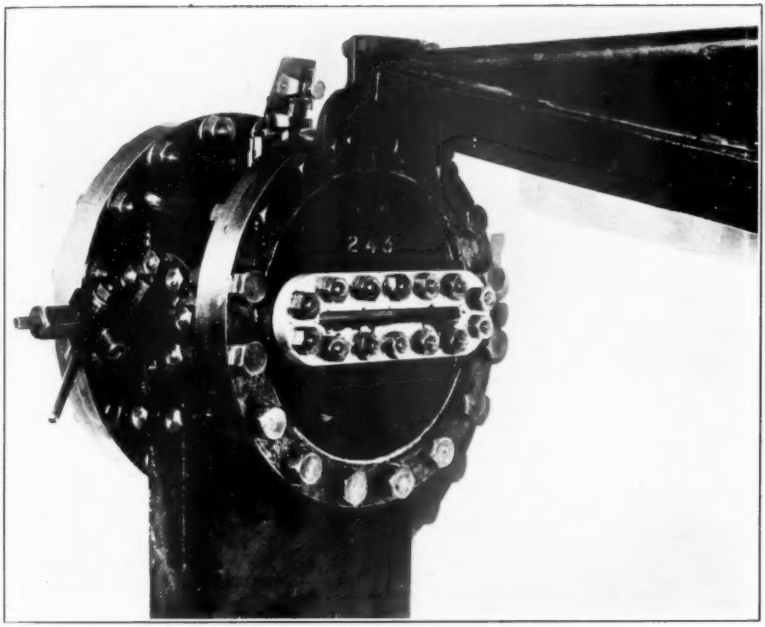


This assumption has recently been challenged. Wheeler (J., 1918, **113**, 840) obtained experimental proof of the fact that in mixtures of methane and air containing between 7·5 and 12·5% of methane, ignited at the centre of a spherical bomb of 4 litres capacity, the times taken for the attainment of maximum pressure (measured from the moment of ignition) synchronised with the times taken for the flame to reach the walls; but the measurements of the last-named time-intervals were made by means of a "screen-wire" method which might have involved an indeterminate experimental error. It seemed desirable, therefore, to attempt direct synchronisation of the rate of development of pressure and the rate of spread of flame in an explosive mixture by simultaneous photographic registration on a rapidly revolving drum.

The apparatus devised for our purpose consists of an explosion-vessel (Plate I) of phosphor-bronze, the interior of which can be rendered spherical or cubical at will, fitted with windows through which the flame can be photographed and with a pressure-gauge of the diaphragm type.

* Meaning, thereby, the complete spread of flame throughout the vessel, but not necessarily complete combustion.

PLATE I.



[*To face p.* 154.]

The pressure-gauge (Fig. 1), which is a modification of that designed by Rice (*U. S. Bureau of Mines, Bull. No.* 167, p. 51, 1922), has an optical indicator which is so arranged as to throw a spot of light on the same revolving drum as is used for obtaining a photographic record of the movement of the flame. The diaphragm, A, is of steel, 0·051 mm. thick, gold-plated to resist corrosion, and fitted flush with the inner surface of the explosion-vessel. It forms the base of a cylinder, B, of 34·92 mm. diameter, machined from tool-steel and having a thick collar to avoid distortion when clamped firmly in position by the flanged plug, C. Through a hole in this plug passes a rod, D, 1·59 mm. in diameter, one end of which is in contact with the diaphragm, the other being attached to a bell-and-crank lever which bears against a lever carrying a small mirror.

For the experiments described in this paper, the explosive mixtures were of carbon monoxide and air, saturated with water vapour at 19°. Ignition was effected exactly at the centre of the vessel by means of a secondary discharge at a 1·5 mm. spark-gap between platinum electrodes sheathed side by side within a glass rod of 3 mm. diameter. This rod fitted into a recess in an insulating plug of bakelite in the wall of the vessel, suitable electrical connexions to the electrodes being made through it to terminals outside.

Explosions within a Sphere.—The spherical cavity of the explosion-vessel was 14·8 cm. in diameter. In order to obtain a photograph of the flame within it, a slit, 2 mm. wide, was cut half-way through the walls horizontally from the window. There were thus left two thin, fin-shaped slots in the sides of the casting abutting on the window, in which, as appears in the photographs, flame was forced during the explosions. When the camera lens was focussed on the spark-gap, there was obtained during an explosion a record on the revolving drum of the movement of the flame in a horizontal plane in both directions from the spark. Such a photograph of the flame in a 60% carbon monoxide–air mixture is reproduced (reduced in size) on Plate II. The boundary of the spherical cavity is indicated on this photograph by the parallel lines drawn thereon as projections from the slit shown diagrammatically at the bottom. The flame forced (towards the camera and therefore out of focus) into the fin-shaped slots previously mentioned, appears as a collar around the upper part of the record. It will be noticed, also, that the image of the flame is divided equally into portions of different densities. This is due to the flame being partly obscured by the glass rod covering the electrodes.

The record also bears the time–pressure chart. It will be seen that the moment of attainment of maximum pressure corresponds

almost exactly with the moment at which the flame reached the sides of the vessel.

Measurements made from this and similar records obtained with other mixtures of carbon monoxide and air are summarised in Table I.

TABLE I.

Explosions of Carbon Monoxide and Air within a Sphere.
(*Mixtures Saturated with Water-vapour at* 19°.)

	Time-intervals (in 1/100ths of a second).		
CO (%).	(1) Between ignition and attainment of maximum pressure.	(2) Between ignition and flame reaching boundary of sphere on horizontal axis.	Difference between (1) and (2).
20·25	17·17	16·02	+1·15
25·05	9·10	9·08	+0·02
29·40	6·40	6·38	+0·02
39·90	4·56	4·56	±0·00
45·25	4·24	4·28	−0·04
50·10	4·51	4·50	+0·01
58·70	5·18	5·20	−0·02
69·30	11·61	11·16	+0·45
74·00	24·44	20·28	+4·16

It is clear from these results that with all mixtures save those in which the flame-front travelled very slowly (mixtures containing less than about 25% or more than about 65% of carbon monoxide) the moment of maximum pressure coincides, within less than half a millisecond, with the arrival of the flame-front at the boundary of the vessel. When the flame-front travels so slowly that its movement is affected by convection, it reaches the top of the vessel, and can be seen at the ends of the window along the horizontal diameter, whilst there is still a considerable volume of mixture in the lower part of the vessel through which it has not travelled. The pressure therefore continues to rise after the flame has reached the boundary of the sphere on its horizontal axis.

Explosions within a Cube.—By removing two shaped castings of phosphor-bronze from within the casing of the explosion-vessel, a cubical cavity of 15 cm. edge was produced, the arrangement of manometer diaphragm, firing electrodes, and horizontal window remaining the same as when the cavity was spherical, except that the window now had an effective width of 4 mm. In addition, the removal of the castings that had formed the spherical cavity uncovered a window 4 mm. wide, which passed diagonally from corner to corner across the face of the cube opposite to that in which the horizontal window was fitted. By an arrangement of interconnected chain-gearing, simultaneous photographs, on two revolving drums, could be taken of the flame-front as it moved from the

centre of the cube (*a*) towards the walls and (*b*) towards the corners. The time–pressure chart was recorded only on the drum used for photographing the horizontal window.

Mixtures of carbon monoxide and air were used similar to those when the cavity was spherical. Typical records, obtained with a mixture containing 60% of carbon monoxide, are reproduced on Plate III (these are reduced in size, but not in the same proportion as for Plate II). When interpreting these records, the lenses of both cameras, which were focussed on the igniting spark, may be regarded as looking into the interior of the bomb from either side, the one through a horizontal and the other through a diagonal window.

Considering first the record obtained through the horizontal window (*a*, Plate III): The lens will "see" best of all the flame as it travels across a vertical plane through the spark-gap, on which the lens has been focussed. Nearer, and in less accurate focus, it will see the front edges of the two sides of the cavity. Farther away, and in better but not perfect focus, it will see the two-sided corners formed by the sides and back of the cavity. The two pairs of curved V-shapes on the record show the progress of the flame after it has reached the sides of the cavity and is travelling (the outer pair) towards the front corners and (the inner pair) towards the back corners.

In the photograph obtained through the diagonal window, the lens "sees" four three-sided corners and the record shows the times at which the flame reaches, (i) and (ii), the upper and lower near corners of the cube (the outer "horns" in the photograph), and (iii) and (iv), the upper and lower far corners (the inner horns).

Measurements obtained from series of photographs similar to those reproduced on Plate III are recorded in Table II. From these measurements it is apparent that pressure continues to be developed slowly after the flame-front has touched the walls of the cube and whilst it is squeezing itself into the corners.* Thus the moment of attainment of maximum pressure when the explosion-vessel is cubical does not synchronise exactly, even when ignition is central, with the moment of "complete inflammation" of the mixture, but is antecedent to it, no doubt because, whilst the flame-front at each of the eight corners is nearing the end of its journey, there is considerable cooling of the gases, burnt earlier during the explosion, at the faces of the cube.

A comparison of the time–pressure charts obtained with the same mixture (60% carbon monoxide in air) exploded in the two

* The photographs reproduced on Plate II of our paper (J., 1925, **127**, 764) help to explain why this should be so.

TABLE II.

Explosions of Carbon Monoxide and Air within a Cube.
(*Mixtures Saturated with Water-vapour at* 19°.)

	Time-intervals, measured from time of ignition (in 1/100ths of a second).				
CO (%).	Attainment of maximum pressure.	Flame at sides (see *a*, Plate III).	Flame at two-sided corners (see *a*, Plate III).	Flame at top corners (see *b*, Plate III).	Flame at bottom corners (see *b*, Plate III).
20·30	22·86	6·7	19·75	21·36	25·25
30·20	7·78	4·9	6·84	8·28	8·58
40·20	6·04	4·0	5·32	6·49	6·56
45·20	5·70	3·9	4·98	6·13	6·13
50·00	6·09	4·2	5·40	6·46	6·69
60·40	8·64	5·7	7·65	9·39	9·78
69·55	25·02	10·2	20·64	22·44	27·50

shapes of vessel (see Plates II and III) brings out clearly the extent to which cooling occurs during the development of pressure when part of the flame-front can touch a cold metal surface whilst the remainder is still travelling through part of the mixture. It will be seen also that the character of the "cooling-curve" is affected by the shape of the explosion-vessel. In this connexion, we would emphasise our previous observation (*loc. cit.*, p. 767) that, when attempting to interpret the character of time–pressure curves obtained from gaseous explosions in closed vessels, due consideration must be paid to the shape of the vessels and to the position of the point of ignition.

This work forms part of a research that we are carrying out for the Safety in Mines Research Board, to whom our thanks are due for permission to publish this paper.

SAFETY IN MINES RESEARCH LABORATORIES,
SHEFFIELD. [*Received, October 15th*, 1926.]

XXVII.—*Molecular Structure in Solution. Part I. The Densities and Viscosities of Aqueous Solutions of Cobalt Chloride and Hydrochloric Acid.*

By OWEN RHYS HOWELL.

THE red and blue colours of the cobaltous compounds and the change from one to the other have been the subject of many investigations. The latest work is that of Hill and Howell (*Phil. Mag.*, 1924, **48**, 833), where a fairly full account of previous work will be found.

These authors examined the absorption spectra in the visible region of a number of cobaltous solutions and solid pigments. They showed that the spectra of the red solutions were precisely similar to those of the red pigments, and the spectra of the blue solutions to those of the blue pigments. In the *red* pigments, the cobalt atom replaced the atom of another metal known from *X*-ray examination of the crystal structure to be surrounded by *six* other atoms, whilst in the *blue* pigments it replaced an atom similarly known to be surrounded by *four* other atoms. The conclusion was therefore drawn that in the red solutions the cobalt atom is surrounded by six other atoms or groups, whilst in the blue solutions it is surrounded by four. The suggestion was made that a definite association of groups or a molecular structure exists in solution, just as in solids. Thus in the dilute aqueous solution of any cobaltous salt, which is red, the cobalt atom is in association with six water molecules, whilst in the blue solution of cobalt oxide in potash it is in association with four groups, possibly hydroxylic.

Support for this view is found in the work of French and Lowry (*Proc. Roy. Soc.*, 1924, *A*, **106**, 489). These authors examined the absorption spectra of a number of cupric salts in different solvents, and showed that they all consisted essentially of one band in the infra-red or red, which was due to the cupric atom, and another in the ultra-violet, which depended on the other part of the molecule. Since the cupric atom gives only one band (which, however, varies in position with the nature of the compound), the authors concluded that the cupric atom is similarly associated in all the solutions. Since many of the salts examined were the cupric salts of organic acids, which are known to be co-ordinated compounds, the conclusion was drawn that in solution the cupric atom is always associated with four other atoms or groups. Although many of the co-ordinated compounds are stable in aqueous solution, others are decomposed. The spectrum, however, is of the same type, and it is therefore concluded that in these solutions, and in dilute aqueous solutions of simple cupric salts, the cupric atom is surrounded by four molecules of water.

In the present paper, an account is given of work which throws further light on the existence of a molecular structure in solution. It deals with the change in colour from red to blue on adding hydrochloric acid to an aqueous solution of cobalt chloride. The densities and viscosities of a series of solutions, having the same concentration of cobalt chloride but increasing concentrations of hydrochloric acid, have been measured. The same properties for an exactly similar series of solutions without cobalt have also been evaluated,

and from the differences in the values for corresponding solutions it is possible to follow the change which takes place in the state of the cobaltous atom. It is suggested that in the aqueous solution, the cobalt is present as hydrated ions, $Co(H_2O)_6^{\cdot\cdot}$, where the cobalt atom is surrounded by six groups, and that as the concentration of hydrochloric acid is increased, these are progressively converted into ions where the cobalt is surrounded by four groups, probably the complex ions, $CoCl_4''$. The existence of complex cobaltous ions in solution is discussed by Hantzsch and Shibata (*Z. anorg. Chem.*, 1912, **73**, 309) and by Kotschubei (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1055).

Experimental.

Determination of Density.—The determination of the density of a liquid is more rapidly and conveniently made with an ordinary specific-gravity bottle than with a pyknometer. Carefully used, this bottle gives reproducible and accurate results. One source of error lies in replacing the stopper in different positions. This was avoided by making a small file mark on the neck of the bottle and on the stopper, and replacing the stopper for each determination so that the marks were in line. Another and more serious error is due to evaporation, which occurs, not only through the hole in the stopper, but more especially through the ground joint. Even when the hole in the stopper is effectively closed, there is a continuous loss in weight so long as the liquid in the bottle is in contact with any portion of the ground surfaces. It would appear that the liquid rises in the fine channels between the roughened faces, and thus reaches the outside round the stopper, where it evaporates. All evaporation is completely prevented by placing over the stopper and the neck of the bottle a small cap, made from glass tubing, which rests on the shoulders of the bottle. Protected in this way, a bottle full of aqueous solution remains unchanged in weight for many hours.

All determinations of density were made with a density bottle of about 25 c.c. capacity, the precautions described above being taken. The relative density was calculated from the formula

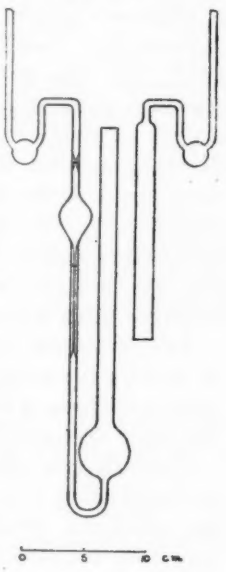
$$d^{20°}_{20°} = W'/W - 0{\cdot}0012(W' - W)/W,$$

where W = weight of water filling the bottle, W' = weight of solution filling the bottle, and 0·0012 = mean density of air. The maximum error in the determinations is less than one unit in the fourth place of decimals.

Determination of Viscosity.—The viscosity measurements were made in a viscometer of the Ostwald type. In order to provide against evaporation and loss of gas from the strongly acidic solutions

(especially at the higher temperatures at which further measurements will be made), a simplified modification of the apparatus used by Findlay (*Z. physikal. Chem.*, 1912, **79**, 97) was specially made. The viscometer is shown in Fig. 1. It consists of two parts, one being precisely similar to the Ostwald viscometer. The volume of the upper bulb is about 10 c.c. and the diameter of the capillary about 0·4 mm. The narrow limb is continued to form a U-tube with a small bulb of about 2 c.c. capacity. The other part consists of a tube which just fits over the broad limb of the viscometer and is also provided with an exactly similar U-tube. The two parts are held together by a rubber band. This arrangement is simpler and more satisfactory than one having a ground joint as no lubricating material is employed and no contamination of the solution is possible.

FIG. 1.



The apparatus is easily taken apart for emptying and cleaning. It was initially thoroughly cleansed with chromic acid, and thereafter rinsed with distilled water after each experiment. It was dried by drawing through it a stream of air, filtered through cotton-wool and dried by concentrated sulphuric acid and calcium chloride. With this treatment alone, it was found that after several determinations concordant results ceased to be obtained and this was traced to the presence of grease. The apparatus was therefore also washed with a little pure alcohol or acetone, filtered while boiling.

A determination of viscosity was made as follows: The small bulbs on the U-tubes were about half-filled with the solution. A fixed amount (16 c.c.) of solution was pipetted into the viscometer. The two portions were assembled, and the apparatus was slipped into two clips fastened to a bar clamped upright in the thermostat. It was thus ensured that the apparatus was perfectly vertical for each experiment. The apparatus was immersed so that only the open ends of the U-pieces were above water. The solution in the small bulbs being under the same conditions as that in the apparatus, and all interchange of air having to take place through the bulbs, the solution under examination suffers no change in composition. It was found that perfectly concordant values were obtained for a large number of consecutive measurements or at long intervals.

The time of flow was measured by means of a stop-watch reading

to $\frac{1}{5}$ of a second. The time for water was 376·6 seconds, and this was checked at intervals throughout the measurements and found to be exactly reproducible. All the solutions examined had a time of flow greater than this, so that the maximum error in the determinations of viscosity is less than about 0·05%. In calculating the viscosity coefficient, the value $\eta_{20°} = 0{\cdot}01005$ for water was used.

Materials. The water used for determining the water constant of the viscometer and for making up the solutions was laboratory-distilled water, filtered, and twice re-distilled with precautions to preclude contamination by dust or grease. The hydrochloric acid was the pure commercial product, and the cobalt chloride was Kahlbaum's purest, free from iron and nickel.

Solutions. Two stock solutions were prepared, one containing 120 g. per litre of $CoCl_2,6H_2O$ in water, and the other containing the same amount per litre in concentrated hydrochloric acid. The acidity of this solution was found to be 10·63*N* by diluting and titrating against standard sodium hydroxide. From these two solutions a series of solutions was made, each having the same concentration of cobalt chloride, but varying concentrations of hydrochloric acid. This was done by taking x c.c. of the aqueous solution and $(50 - x)$ c.c. of the acid solution, and making up to 50 c.c. with water.

An exactly similar series of solutions containing the same amounts of acid as the foregoing, but no cobalt, was made in precisely the same way from water and a stock solution of hydrochloric acid of the same strength as above (10·63*N*).

Carefully graduated vessels were used in all cases and the error in composition does not exceed 0·1%. The volumetric handling of the solutions, necessitating the largest error in this work, consequently imposes the limit on the accuracy of the measurements of their densities and viscosities.

All measurements were made in a thermostat, with glass front and back, regulated to $20° \pm 0{\cdot}01°$.

Results.

Densities.—The relative densities of the two series of solutions, determined as described, are given in Table I. Many previous determinations of the density of hydrochloric acid solutions have been made over a wide range of concentration (see, *e.g.*, Pickering, *Ber.*, 1893, **26**, 277; Lunge and Marchlewski, *Z. angew. Chem.*, 1891, **4**, 133; Lunge, "Technical Chemists' Handbook"). As most of these investigators have expressed their results as absolute densities ($d_4^{t°}$), the values now found are also given in the same

TABLE I.

Densities.

1. Normality of acid, N.	2. Relative density of $CoCl_2 + HCl$, $d^{20°}_{20°}$.	3. Relative density of HCl alone, $d^{20°}_{20°}$.	4. Relative density (calc.).	5. Absolute density, $d^{20°}_{4°}$.	6. Density difference (2—3).
0	1·0582	1·0000	*1·0000*	*0·9982*	0·0582
1·063	1·0755	1·0186	*1·0182*	*1·0168*	0·0569
2·126	1·0926	1·0364	*1·0361*	*1·0346*	0·0562
3·189	1·1092	1·0536	*1·0536*	*1·0518*	0·0556
4·252	1·1261	1·0707	*1·0707*	*1·0689*	0·0554
5·315	1·1420	1·0871	*1·0874*	*1·0852*	0·0549
6·38	1·1575	1·1036	*1·1038*	*1·1016*	0·0539
6·59	1·1602	1·1067	*1·1070*	*1·1048*	0·0535
6·91	1·1639	1·1112	*1·1119*	*1·1093*	0·0527
7·23	1·1678	1·1162	*1·1167*	*1·1142*	0·0516
7·44	1·1704	1·1195	*1·1198*	*1·1176*	0·0509
8·50	1·1830	1·1355	*1·1355*	*1·1337*	0·0475
9·57	1·1957	1·1507	*1·1507*	*1·1488*	0·0450
10·63	1·2100	1·1657	*1·1656*	*1·1637*	0·0443

form in col. 5 of Table I for the sake of comparison. They agree closely with those already reported in the literature.

The values of the relative densities are plotted against the concentration of acid for the two series of solutions in Fig. 2A. It is seen that the curve for the solutions of acid only is a smooth one. As for most aqueous solutions, the relative density is expressed approximately by an equation of the form

$$d_{\text{solution}} = d_{\text{water}} + xN + yN^2,$$

where x and y are constants, and N is the normality of the solution. Putting $x = 0{\cdot}017321$ and $y = -0{\cdot}00016316$, the values calculated from the expression are given in col. 4 of Table I. Comparing them with the observed values in col. 3, it is seen that the agreement is very fair throughout the range. Better agreement is not obtained by inserting a cubic term in the expression.

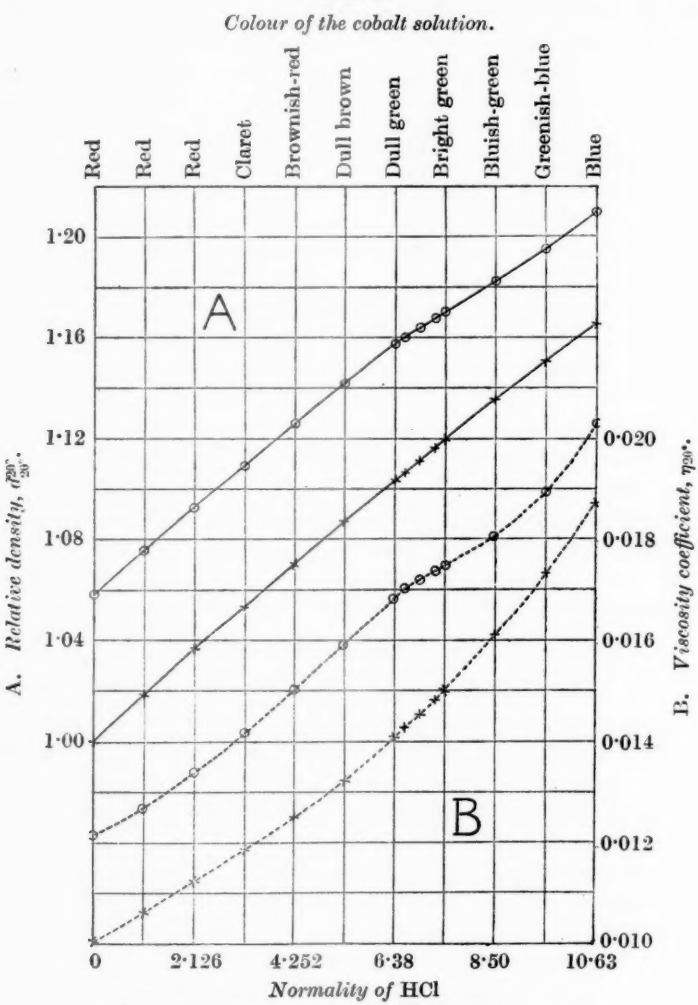
The curve for the solutions containing cobalt, on the other hand, is not smooth. It consists of two parts, one (for the lower values) being convex and the other concave to the line joining the extreme values. The break in the curve is obvious. It occurs after the maximum colour change, and this circumstance is discussed later.

Many measurements are on record showing breaks in density and viscosity curves, and theoretical conclusions have been drawn from such breaks alone. In the present instance, however, it is possible, not only to obtain more detailed and trustworthy evidence, but also to follow the course of the change which is the cause of the break.

By subtracting the values for the acid alone from the values for

the solutions of cobalt chloride and hydrochloric acid the influence of the cobalt atom on the molecular structure of the solution is

FIG. 2.



A. (*Full line curves*). *Relative density.*
B. (*Dotted line curves*). *Viscosity coefficient.*

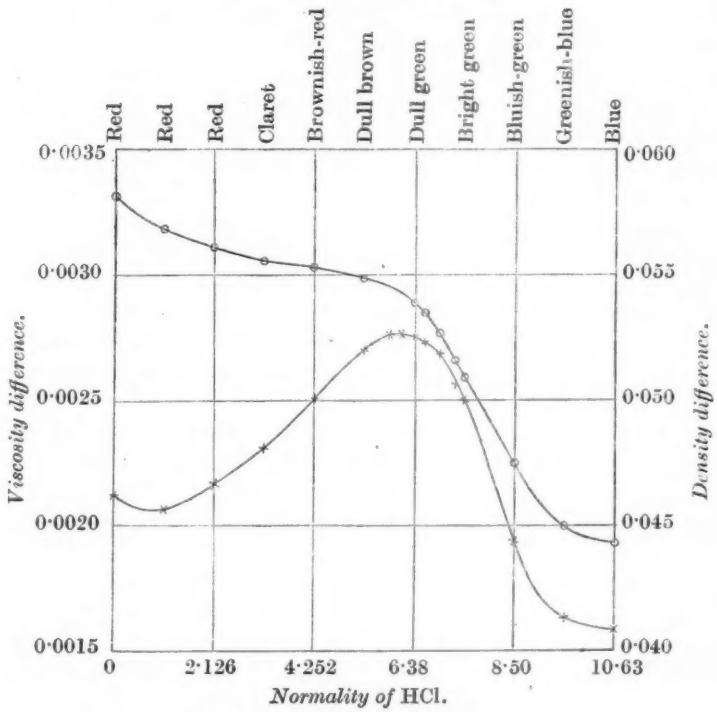
Solutions of hydrochloric acid + cobalt chloride shown thus, ⊙.
Solutions of hydrochloric acid only shown thus, ×.

brought to light. If the arrangement of the atoms or groups around the cobalt atom were the same, whatever the concentration of acid present, the two curves should be parallel and the difference between

the values for corresponding solutions in the two series should evidently be constant.

These values are given in col. 6 of Table I, and are hereafter referred to as density differences, for brevity. It is seen that they vary continuously with the concentration of the acid. The differences are plotted against the concentration of acid in Fig. 3, and the curve can be fully interpreted in the light of the theory already given.

FIG. 3.



Upper curve : density differences.
Lower curve : viscosity differences.

In the aqueous solution, the cobalt chloride is largely ionised. The cobalt ions are hydrated with six molecules of water, and the solution is therefore red. As the solution is made increasingly acidic, this structure is broken down. The water molecules are crowded out by chlorine ions, and the cobalt atom becomes eventually surrounded by four chlorine atoms, the solution then being blue. Since the final value for the density difference is less than the initial value, the "four"-packing must be less dense than the

"six." There should be a continuous diminution of the difference in density as the change proceeds from the red to the blue form, and this is seen to be so, for the curve falls along its entire course. When the change is complete, further increase in the concentration of acid should have no further effect, *i.e.*, the difference in density between the cobalt solution and one containing the same amount of acid only should become and remain constant. It is seen that this state has practically been reached at the highest concentration of acid employed, for the curve is rapidly flattening out to become parallel to the axis of hydrochloric acid concentration.

It is seen that the diminution of the difference in density, although continuous, does not take place evenly throughout the change from red to blue. The change is at first very gradual, and then (at a point corresponding to the abrupt change in the viscosity-differences curve, which will be discussed later) it takes place very rapidly. This also is explicable and is attributed to two causes.

First, as the change from the six- to the four-packing proceeds, the balance between the undissociated cobalt chloride and its ions is disturbed, and more salt therefore becomes ionised. The newly-liberated cobalt ions are immediately hydrated. The water used up for this purpose was previously free, but is now bound in close union with the cobalt atom, thus making the solution denser and counteracting the diminution due to the formation of the four- from the six-packing.

Secondly, and more important, is the effect of the electrical attraction between the ions. The $Co(H_2O)_6^{\cdot\cdot}$ ions present in the aqueous solution carry a double positive charge. The $CoCl_4''$ ions produced by the action of the acid carry a double negative charge. As the concentration of acid is increased, the amount of the negatively charged ion also increases. There will evidently be a great attraction between these oppositely charged ions. This will result in a closer association of the constituents of the solution, tending to make it more dense and thus counteracting the general diminution in density due to the looser packing of the four- than the six-grouping. This effect will continue to become more and more marked until the amounts of both ions present are the same, when the attraction between them will be a maximum. It is seen that, for the first part of its course, the curve does actually become increasingly less steep.

After one-half of the cobalt ions have undergone the change from the sixfold to the fourfold association, continued increase in the strength of the acid produces a far greater diminution in the density difference. The continued production of $CoCl_4''$ ions from the $Co(H_2O)_6^{\cdot\cdot}$ ions not only causes, in itself, a diminution of the density

difference, but, whereas it formerly increased the attraction between the two kinds of ions by making their number more nearly equal, and thus tended to counterbalance the decrease in the density difference, it now makes the numbers of the two kinds of ions more and more unequal, thus lessening the attraction between them and causing the density difference to decrease far more rapidly. It is seen that the curve which begins by falling less and less steeply now falls extremely sharply.

It is therefore suggested that the point at which the curve undergoes inflexion corresponds (very approximately) to a solution having equal amounts of the two kinds of ions, *i.e.*, having equal numbers of cobalt atoms with the six- and four-groupings.

It is to be noted that this point does not correspond with the maximum colour change. The solution has already changed colour before the curve exhibits inflexion. This is in accordance with the fact already pointed out by Hill and Howell (*loc. cit.*) that the absorption spectra of blue cobalt solutions show that both forms (red and blue) may be present together. Thus the absorption spectrum of cobalt chloride in magnesium chloride solution clearly shows the presence of the red association although the solution appears quite blue. Indeed, since the blue form is far more intense than the red, the solution may have considerably more of the red form than of the blue, and still be perfectly blue to the eye. In the present instance, it is seen clearly that the colour change has already taken place before even half of the cobalt has changed from the six- to the four-association.

Viscosities.—The viscosity coefficients of the two series of solutions, determined as already described, are in Table II. Previous determinations of the viscosity of solutions of hydrochloric acid alone have been made by Reyher (*Z. physikal. Chem.*, 1888, **2**, 744), and of aqueous solutions of cobalt chloride alone by Wagner (*ibid.*, 1890, **5**, 31) and by Green (J., 1908, **93**, 2023).

The results given in Table II are plotted in Fig. 2B. It is seen that the values for hydrochloric acid lie on a perfectly smooth curve, which, however, cannot be even approximately represented by an expression of the type found to hold good for the density curve, or by one having a cubic term.

The curve for cobalt chloride and hydrochloric acid evidently consists of two distinct parts, both of which are concave to the line joining the extreme values. The break occurs at precisely the same concentration as that in the corresponding density curve, and is far more pronounced. If the cobalt atom were similarly associated in all these solutions, the two curves should be parallel, *i.e.*, the viscosity differences should be constant.

TABLE II.

Viscosities.

1. Normality of acid, N.	2. Viscosity coeff. of $CoCl_2$ + HCl, $\eta_{20°}$.	3. Viscosity coeff. of HCl alone, $\eta_{20°}$.	4. Viscosity difference (2—3).
0	0·01218	0·01005	0·00213
1·063	0·01272	0·01065	0·00207
2·126	0·01342	0·01125	0·00217
3·189	0·01418	0·01187	0·00231
4·252	0·01502	0·01251	0·00251
5·315	0·01593	0·01323	0·00270
* 5·85	0·01640	0·01364	0·00276
* 6·11	0·01662	0·01386	0·00276
6·38	0·01683	0·01408	0·00275
6·59	0·01703	0·01430	0·00273
6·91	0·01721	0·01452	0·00269
7·23	0·01738	0·01482	0·00256
7·44	0·01750	0·01500	0·00250
8·50	0·01805	0·01611	0·00194
9·57	0·01894	0·01731	0·00163
10·63	0·02028	0·01870	0·00158

* The values of the viscosity coefficients for these two concentrations are read from the viscosity curves shown in Fig. 2B.

It is seen, however, from the values of the viscosity differences, given in col. 4 of Table II, that they show a remarkable variation. The values are plotted against the normality of the acid in Fig. 3. The curve first exhibits a very small dip. The first effect of the acid on the solution is to decrease the ionisation of the cobalt chloride owing to the addition of a common ion. This results in a decrease of the number of cobalt ions present. These hydrated ions may reasonably be assumed to be comparatively highly viscous and the reduction in their number therefore leads to an initial decrease in the viscosity difference.

This initial effect of the acid is, however, soon overwhelmed by the increase in ionisation resulting from the transformation of the $Co(H_2O)_6^{\cdot\cdot}$ ions into $CoCl_4''$ ions by the action of the acid. The presence of these two kinds of ions, oppositely charged, causes an increase in the viscosity of the solution. Their electric fields, causing a strong attraction between them, retard their movement past one another, thus causing the solution to become more viscous. Increase in the concentration of the acid causes further transformation of the one type of ion into the other. The viscosity-differences curve therefore rises rapidly, and this in spite of the fact that the corresponding density curve is falling. As already noted when discussing the density changes, the attraction between the ions should be a maximum when there are equal numbers of each. It is seen that the curve rises to a maximum. It is suggested that at the maximum there are equal numbers of the two kinds of ions

present, and it should be noted that the maximum in the viscosity-differences curve corresponds exactly with the point of inflexion in the density-differences curve, which was accounted for by the same reasoning.

Continued increase in the concentration of acid causes continued transformation of the cobalt atom from the six- to the four-packing. This results in the number of ions of each kind becoming increasingly unequal, in the attraction between them becoming thereby diminished, and therefore in the viscosity difference decreasing continuously. It is seen that the curve falls sharply from the maximum.

When the whole of the cobalt has assumed the new configuration, further increase in the concentration of the acid should produce no change in the viscosity difference. It is seen that, as with the density-differences curve, so also the viscosity-differences curve flattens out and indicates that, with the highest concentration of acid employed, the change to the four-configuration is practically complete.

It is also to be noted that whilst the density-differences curve indicates that the density of the four-configuration is less than that of the six-, the viscosity-differences curve shows that its viscosity is also less.

It is proposed to make further similar measurements at different temperatures and with different concentrations of cobalt, and also to determine other physical constants for these solutions.

Summary.

1. The densities and viscosities of a series of aqueous solutions containing a constant amount of cobalt chloride and varying amounts of hydrochloric acid have been determined.

2. The densities and viscosities of an exactly similar series containing hydrochloric acid only have also been measured.

3. From the differences in values for corresponding solutions, the effect of the acid on the cobalt in solution can be followed.

4. The curve showing the differences in density exhibits a point of inflexion, and that showing the differences in viscosity a maximum, both well-defined and at the same concentration of acid.

5. The general form of the curves and these two important characteristics are explained by attributing the action of the acid to the forcing of the cobalt atom out of its association with six molecules of water into an association with four atoms of chlorine.

6. The change of colour from red to blue and the point at which it occurs are accounted for.

The author would express his thanks to Prof. Alex. McKenzie, F.R.S., for giving him every facility for prosecuting this work.

UNIVERSITY COLLEGE, DUNDEE.
UNIVERSITY OF ST. ANDREWS. [*Received, October 4th*, 1926.]

XXVIII.—*The Interaction of Potassium* m-*Tolyloxide with Aliphatic Esters in Aqueous–Alcoholic Solutions.*

By ERNEST LESTER SMITH.

THIS research is an extension of the work of Gyngell (J., 1926, 2484; and private communication) on the interaction of potassium phenoxide with aliphatic esters in alcoholic solutions. The present reaction is shown to take the same course as the former: The water in the aqueous alcohol hydrolyses the potassium tolyloxide, with formation of cresol and potassium hydroxide; the latter then hydrolyses the ester. This hypothesis led to an expression for the velocity coefficient which was satisfactory within the limits of experimental error. Thus, we have

$$\underset{(c-x-y)}{CH_3{\cdot}C_6H_4{\cdot}OK} + H_2O \rightleftharpoons \underset{(b-x-y)}{CH_3{\cdot}C_6H_4{\cdot}OH} + \underset{(d+x+y)}{KOH} \quad \underset{y}{}$$

$$\underset{(a-x)}{CH_3{\cdot}CO_2Et} + \underset{y}{KOH} \longrightarrow \underset{x}{CH_3{\cdot}CO_2K} + EtOH$$

where a, b, c, and d are the initial concentrations of ester, water, tolyloxide, and cresol, respectively, and x is the amount of potassium acetate formed and y the amount of free potassium hydroxide present at time t, the concentrations of the reacting molecules being as shown. For equilibrium

$$K(c-x-y)(b-x-y) = (d+x+y)y \quad . \quad . \quad (1)$$

where K is the equilibrium constant. For the second reaction

$$dx/dt = k(a-x)y \quad . \quad . \quad . \quad . \quad . \quad (2)$$

k being the velocity coefficient. It must now be assumed that y is always very small compared with x, *i.e.*, that the alkali formed by hydrolysis is always at a negligibly small concentration. Eliminating y, we obtain

$$dx/dt = Kk(a-x)(b-x)(c-x)/(d+x) \quad . \quad . \quad (3)$$

which on integration yields

$$Kk(t_2-t_1) = \frac{(d+a)}{(b-a)(c-a)}\log_e\frac{(a-x_1)}{(a-x_2)} + \frac{(d+b)}{(a-b)(c-b)}\log_e\frac{(b-x_1)}{(b-x_2)} + \frac{(d+c)}{(a-c)(b-c)}\log_e\frac{(c-x_1)}{(c-x_2)} \quad . \quad . \quad . \quad . \quad (4)$$

t_1 and x_1 corresponding to the earliest determinable time and titre, respectively, and t_2 and x_2 to subsequent determinations.

Simplification can be effected for two special cases: (*a*) When ester and tolyloxide are present in equivalent proportions, *i.e.*, $a = c$,

$$Kk(t_2 - t_1) = \frac{(d+a)(x_2-x_1)}{(b-a)(a-x_1)(a-x_2)} + \frac{(d+b)}{(b-a)^2} \log_e \frac{(b-x_1)(a-x_2)}{(b-x_2)(a-x_1)} \quad (5)$$

and (*b*) when, in addition, water is in such large excess as to be virtually constant,

$$Kk(t_2 - t_1) = \frac{(d+a)(x_2-x_1)}{b(a-x_1)(a-x_2)} - \frac{1}{b} \log_e \frac{(a-x_1)}{(a-x_2)} \quad . \quad (6)$$

The reaction between potassium *m*-tolyloxide and ethyl acetate proceeded somewhat more rapidly than that with potassium phenoxide under the same conditions. On application of formula (5), with $x_1 = 0$, $t_1 = 0$, values were obtained for Kk which were sensibly constant. Further experiments, in which the concentrations of the reactants and also the temperature have been varied between wide limits, have yielded values for kK in which the maximum deviation from the mean usually lies between 2 and 5%; this can be ascribed to experimental error, since the deviations are irregular.

The following experiment is typical, time being expressed in minutes and concentrations in milliequivs. per litre.

TABLE I.

Potassium *m*-tolyloxide, $N/2$. Temperature 70°.
Ethyl acetate, $N/2$. Water = 10% of total.

Time.	Titre.	% Reaction.	x.	$a - x$.	$b - x$.	$Kk \times 10^4$.
0	20·0	—	—	500	5555	—
5	15·3	23·5	117·5	382·5	5438	—
19	11·75	41·2	206	294	5349	1·64
35	9·95	50·2	251	249	5304	1·65
41	9·6	52·0	260	240	5295	1·58
54	8·65	56·8	284	216	5271	1·64
87	7·25	63·8	319	181	5236	1·62
119	6·3	68·5	342·5	157·5	5213	1·63
125	6·25	68·8	344	156	5211	1·60
					Mean	1·62

The reaction is evidently similar to that investigated by Gyngell (*loc. cit.*). No trace of the *m*-tolyl ether could be detected among the products of reaction. Further, if it proceeded in any way different from that assumed, it is extremely unlikely that constant values for Kk would be obtained from the above formula. For example, it can be shown that any side reaction, occurring to the extent of 1—2% during the course of an experiment, would suffice

to make Kk increase or decrease to the extent of about 10% during the run.

The reciprocal of the time for half-reaction was plotted against water concentration for several series of experiments. In each case, the curve was found to cut the water axis at a point corresponding to a water concentration of half that of the ester and tolyloxide, indicating that the time for half-reaction is infinite for water concentrations below this amount; this result is confirmed by the fact that reaction ceases when the water is entirely consumed.

Tables II, III, IV, and V show the values of Kk obtained with the four esters examined. In the last three tables, the concentration of both the ester and the tolyloxide was $N/4$.

TABLE II.

Reaction with ethyl acetate.

% Water.	Tolyloxide.	Ester.	$Kk \times 10^6$.	
0·27	$N/2$	$N/2$	2·55	
1	,,	,,	2·48	
2·5	,,	,,	2·31	
2·5	,,	,,	2·29	Excess cresol = $N/8$.
2·5	,,	,,	2·48	Excess cresol = $N/4$.
5·2	$N/4$	$N/4$	1·92	
5	,,	,,	1·21	Temp. 64·9°.
5	,,	,,	0·84	Temp. 60·1°.
5	$N/8$	$N/2$	1·70	
5	$N/4$	,,	1·82	
5	$N/2$	,,	2·00	
5	,,	N	1·97	
5	,,	$N/4$	1·98	
7·5	,,	$N/2$	1·85	
9	,,	,,	1·65	
10	,,	,,	1·62	
12	,,	,,	1·50	
15	,,	,,	1·37	
20	,,	,,	1·26	
30	,,	,,	1·17	
100	$N/8$	$N/8$	0·880	
100	,,	,,	0·0240	Temp. 30°.
100	,,	,,	0·0149	Temp. 25°.

TABLE III.

Reaction with *n*-butyl acetate.

% Water ...	1·1	2·7	5·0	7·7	10·0	20·0	30·0	45·0
$kK \times 10^6$ ...	1·23	1·22	1·08	1·04	1·041	0·783	0·652	0·525

TABLE IV.

Reaction with *n*-propyl acetate.

% Water	1	2·5	5	10	15	20
$kK \times 10^6$	2·10	1·90	1·67	1·445	1·265	1·13

TABLE V.

Reaction with methyl acetate.

% Water	1	2·5	5	7·5	10	15	25
$kK \times 10^6$	1·91	1·605	1·40	1·34	1·29	1·31	1·33

Relative Activity of the Esters.—It was to be expected that the values of kK for the different esters would be in the order of their molecular weights, since the esters employed are members of an homologous series. As shown by the tables, however, methyl acetate is abnormal for low percentages of water.

Evaluation of Equilibrium Constant.—The constants obtained are the product of an equilibrium constant and a velocity coefficient. It is obviously desirable to determine the magnitudes of these separately if possible. A method by which this might be achieved, for the reaction in aqueous solution, was the comparison of the rates of hydrolysis of an ester by potassium tolyloxide and by potassium hydroxide, respectively. In the second case, k can be obtained directly, and by substituting this in the value for kK from the first experiment, it is evident that K can be calculated.

Preliminary experiments indicated that the reaction between potassium hydroxide and ethyl acetate was half completed in about 1 minute in the concentrations used, *viz.*, $N/8$ at 30°. As it was desirable to carry out the experiment under these conditions, a special apparatus was designed for the purpose, which is described in the experimental section. The bimolecular coefficients obtained show a maximum deviation from the mean of only 2·5%. The results are as follows :

Concentrations, $N/8$ in aqueous solution. Temperature, 30°. $kK = 0{\cdot}024 \times 10^{-6}$; $k = 0{\cdot}0086$; therefore $K = 2{\cdot}80 \times 10^{-6}$.

A further method by which the value of the equilibrium constant in aqueous solution has been found is by electrometric measurement of the hydrogen-ion concentration in solutions of potassium *m*-tolyloxide. The *E.M.F.* between a hydrogen electrode, immersed in a $N/8$-solution of potassium *m*-tolyloxide, and a saturated calomel electrode was measured by a potentiometer in the usual way. As the p_H is largely affected by a slight excess of either *m*-cresol or potassium hydroxide in the solution, the following procedure was adopted : To the solution were added a few c.c. of potassium hydroxide solution, and the mixture titrated until acid, using a microburette. The curve showed two breaks as anticipated. The first corresponds to the point where cresol and alkali are present in equivalent amounts, and the second more pronounced break to the point where all the alkali has been neutralised. The position of the first break was fixed by a cusp on the first differential curve. *K*

could have been calculated from the voltage at the equivalent point, so found, but for various reasons it was considered preferable to make use of a comparison method. Accordingly, the experiment was repeated, adding $N/10$-potassium hydroxide to $N/8$-potassium chloride solution. The ionisation of the former can be considered the same in solutions of potassium chloride or tolyloxide of the same strength; the alkali concentration is therefore the same in the two solutions when the *E.M.F.* is the same. Hence K can readily be calculated. The results are as follows:

Percentage hydrolysis of potassium *m*-tolyloxide	2·8%.
Equilibrium constant, K,	$1{\cdot}6 \times 10^{-6}$.

These experiments were carried out at 14·5°. Applying the temperature coefficient to the value for K obtained by the previous (kinetic) method, the value at 14·5° is calculated to be $1{\cdot}55 \times 10^{-6}$.

Both these methods appear to be of general application for the determination of the hydrolysis constants of the salts of very weak acids. The dynamical method is probably the more accurate. This value cannot, however, be applied to alcoholic solutions with any certainty, owing to "solvent effect," and it has not been found possible to determine K for alcoholic solutions. The comparison of the rates of hydrolysis of an ester by potassium tolyloxide and by potassium hydroxide is of no value on account of the potassium hydroxide–ethoxide equilibrium, for which the value of the equilibrium constant is at present unknown. Electrometric methods are equally inapplicable.

It will be seen from the tables that in aqueous-alcoholic solutions the value of the composite constant kK decreases with increase in the water concentration. It is, however, impossible to state whether this is due to variation of the velocity coefficient, of the equilibrium constant, or of both.

Alcoholysis of Potassium m-*Tolyloxide.*—In aqueous-alcoholic solutions of potassium *m*-tolyloxide, it is very probable that a certain amount of potassium ethoxide is present in equilibrium with the other components. It can be shown that the extent of this alcoholysis must be very small, since otherwise a more complicated formula would be required in order to give satisfactorily constant values for kK.

Temperature Coefficients.—It can be shown that the value of Q in the Arrhenius equation is the sum of the values for the two reactions:

$$\log_e K_1/K_2 = Q_1(1/T - 1/T')/R$$
$$\log_e k_1/k_2 = Q_2(1/T - 1/T')/R$$

Adding,

$$\log_e k_1K_1/k_2K_2 = (Q_1 + Q_2)(1/T - 1/T')/R$$

The temperature coefficient in alcoholic solution with 5% of water has been measured with the following results :

TABLE VI.

Ethyl acetate, $N/4$. Potassium *m*-tolyloxide, $N/4$.

Temp.	$kK \times 10^6$.	$Q_1 + Q_2$.
60·1°	0·84	
64·9	1·21	17,000
70·0	1·76	16,900
		Mean 16,950

Ratio for 10° rise, 2·1.

The temperature coefficient in aqueous solution has also been measured :

TABLE VII.

Ethyl acetate, $N/8$. Potassium *m*-tolyloxide, $N/8$.

Temp.	$kK \times 10^6$.	$Q_1 + Q_2$.
25·1°	0·0149	
30·0	0·0240	17,200
70·0	0·880	18,500

Q_2, the value of Q for the hydrolysis of ethyl acetate by potassium hydroxide in aqueous solution, has been determined previously. Its value over the range 25—35° is 10,900 calories. If this number be subtracted from the value of $Q_1 + Q_2$ above, for the same range, the result will be Q_1. Hence $Q_1 = 6{,}300$ calories.

Reaction with Other Esters.—Gyngell (*loc. cit.*) has shown that certain esters, notably methyl and ethyl oxalates, react with potassium phenoxide differently from those of the methyl acetate series, giving rise to the corresponding phenyl ether in the same way as the alkyl iodides. The reaction between potassium *m*-tolyloxide and ethyl oxalate in dry alcoholic solution has been investigated. A liquid was obtained identical in properties with *m*-tolyl ether, prepared in the usual way.

Ethyl tartrate and ethyl and propyl formates have also been used. These esters react normally, but more than one hundred times as rapidly as ethyl acetate. After the water in the alcohol has been consumed, a very slow reaction appears to continue, with formation of the tolyl ether. In these cases, the yield was very small, rendering identification difficult.

Gyngell has suggested that the only esters with which this ether formation occurs are those in which no α-hydrogen atom is present. It is, however, difficult to understand how the mere absence of a group can cause a reaction to proceed, or how its presence can inhibit a reaction in which the group concerned takes no part. Moreover, formic and tartaric esters contain one α-hydrogen atom.

A fact much more likely to influence their reactivity is that these esters are all derived from relatively strong organic acids. This suggestion brings these esters into line with those of the common inorganic acids, which all appear to yield the ether readily and are all derived from very strong acids.

Reaction with Ethyl Monochloroacetate.—Monochloroacetic acid is one of the strongest organic acids, and, moreover, it has two α-hydrogen atoms. It therefore seemed of special interest to investigate the behaviour of its ethyl ester with potassium *m*-tolyloxide. The substances reacted very rapidly in dry alcoholic solution, but the main product proved to be a new ester, *ethyl* m-*tolyloxyacetate*:

$$CH_2Cl{\cdot}CO_2Et + C_7H_7{\cdot}OK \longrightarrow KCl + C_7H_7{\cdot}O{\cdot}CH_2{\cdot}CO_2Et.$$

At the same time, a small quantity of the tolyl ether appeared to be formed.

Ethyl *m*-tolyloxyacetate does not appear to have been described previously, although the corresponding acid and some of its other compounds are mentioned by Beilstein. The ester is a colourless, oily liquid with a peculiar characteristic smell; b. p. 264°, with slight decomposition.

Experimental.

Alcohol was dried by refluxing with quick-lime for a few days. During the earlier part of this work, alcohol so treated was deemed to be dry, but later the remaining water was estimated by a method devised by the author, which it is hoped to publish shortly.

Potassium *m*-tolyloxide was prepared in solution only; potassium metal, rapidly freed from oil between filter papers, was added to alcohol under reflux, and the equivalent of *m*-cresol then added. This method of preparing such compounds has been justified by Robertson and Acree (*Amer. Chem. J.*, 1913, **49**, 474) and by Cox (J., 1918, **113**, 670).

In all cases, the desired amount of water was added to the ester solutions, prepared as required. The reaction was carried out in a series of gas-heated thermostats regulated to $\pm 0{\cdot}05°$ by means of mercury-filled thermo-regulators. The reaction vessels consisted of hard-glass test-tubes of about 15 c.c. capacity closed by rubber stoppers. In most cases, 5 c.c. of each solution were pipetted separately into each tube. After shaking, the tubes were transferred to the thermostat and withdrawn at suitable intervals of time, the contents being titrated with standard hydrochloric acid.

The Titration.—The accurate titration of the reaction mixture presents a problem of some difficulty. The mixture consists of

alcohol, unchanged ester, free cresol, and potassium acetate and tolyloxide. The last two substances are salts of a strong base and a weak acid, so that both will be hydrolysed in solution, although to a different extent. In titrating the solution in the usual way, we are treating the potassium tolyloxide as an alkali and the potassium acetate as a neutral salt. Neither assumption is strictly correct. If a solution of the two salts, together with excess alkali, is titrated electrometrically, a curve will be obtained which shows three breaks, corresponding respectively to neutralisation of the free base, of that in the potassium tolyloxide, and of that in the potassium acetate. Consequently, the breaks cover a smaller range of p_H and are much less sharp than in an ordinary titration, and the choice of a suitable indicator is important. The problem is further complicated by the fact that the amount of potassium tolyloxide is decreasing, and potassium acetate increasing, throughout a run. It has been calculated that in a typical experiment the p_H value at the end-point varies from about 6 initially to 8 at three-quarter reaction, the end-point becoming progressively less sharp as the reaction proceeds. Since it is preferable to use the same indicator throughout, it is best to choose one which changes at p_H 7—8. This condition is satisfactorily fulfilled by litmus, provided that the bluish-violet colour is taken to indicate the end-point. These considerations are completely borne out in practice. Litmus is the only indicator, apart from lacmoid, which has been found satisfactory, others changing colour slowly and not at the true end-point.

Measurement of Rapid Reactions.—A simple apparatus was devised for this purpose consisting of a hard-glass boiling tube, with a smaller tube inside of about 12 c.c. capacity. The outer tube was closed by a rubber stopper to which was affixed a piece of stiff wire, bent at the end, which held the inner tube in position. 10 C.c. of one solution were delivered into the inner tube, and 10 c.c. of the other into the outer tube. After being heated in the thermostat for about 15 minutes, the apparatus was inverted once or twice to mix the solutions, then rapidly replaced in the thermostat. After the desired time, the contents were quickly poured into 20 c.c. of cold water containing nearly sufficient acid to neutralise the remaining alkali, the tubes rinsed out, and the titration was completed. By this means, the time error was probably not more than 2 or 3 seconds.

Summary.

1. The velocity of reaction between potassium *m*-tolyloxide and certain aliphatic esters in aqueous–alcoholic solutions has been investigated.

2. It is found that an equilibrium is established between potassium tolyloxide, water, cresol, and potassium hydroxide; the ester is hydrolysed by the last substance.

3. Constants are calculated which are the product of an equilibrium constant and a velocity coefficient.

4. The equilibrium constant in aqueous solution has been evaluated by two methods.

5. The temperature coefficient has been measured in both aqueous and alcoholic solutions.

6. It is found that esters of strong organic acids react very rapidly as above, and they also slowly form the corresponding *m*-tolyl ether.

7. A new ester, ethyl *m*-tolyloxyacetate, is described.

The author wishes to express his thanks to Dr. Crocker for suggesting the line of the research and for his continued interest therein, and to the London County Council for a grant which has enabled the research to be undertaken.

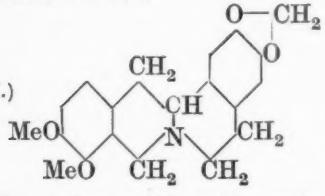
CHELSEA POLYTECHNIC, S.W. [*Received, July 15th*, 1926.]

XXIX.—*Synthetical Experiments on Protopine and Allied Alkaloids. Part I.*

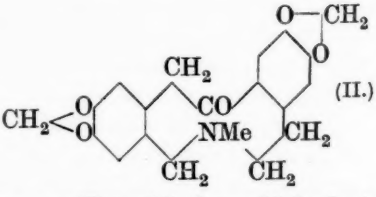
By THOMAS STEVENS STEVENS.

THE present investigation was undertaken with the object of elaborating methods for the production of the ten-membered ring of cryptopine, protopine, and related alkaloids by a direct ring-closure, without previous formation of a structure of the type of tetrahydroberberine (I) (compare Haworth and Perkin, J., 1926, 445, 1769). The synthesis of the isomeride (II) of protopine was first projected, on account of the accessibility of suitable initial materials, and this communication deals with attempts to bring about ring-closure between the carbonyl group and the adjacent benzene nucleus.

(I.)

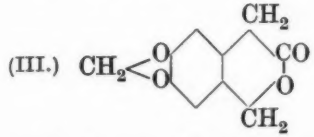


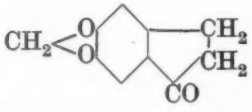
(II.)



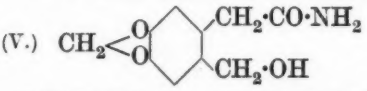
Homopiperonylic acid condenses readily with formaldehyde to give the *lactone* (III) of 6-hydroxymethylhomopiperonylic acid, which was employed as the initial material for the " left-hand half "

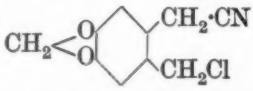
of the molecule (II). The constitution of this lactone was established by oxidation with permanganate, whereby it was converted into the methylenedioxyhomophthalic acid obtained by Perkin and Robinson (J., 1907, **91**, 1086) from 5 : 6-methylenedioxy-1-hydrindone (IV), which latter gives hydrastic acid on oxidation. In the first series of experiments, the lactone was converted by ammonia


(III.)

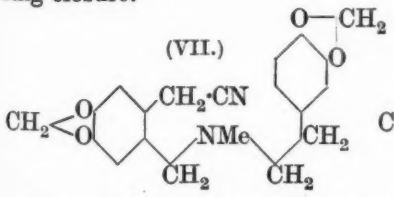

(IV.)

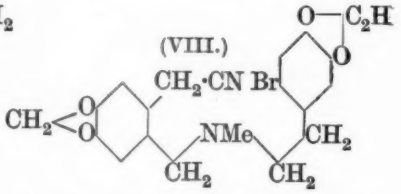
into 6-*hydroxymethylhomopiperonylamide* (V), and the amide treated with phosphorus trichloride, giving 6-*chloromethylhomopiperonylonitrile* (VI). By condensing this nitrile with *N*-methyl-β-piperonylethylamine, N-*methyl*-N-β-*piperonylethyl*-6-*aminomethylhomopiperonylonitrile* (VII) was obtained, but attempts to convert this into (II) by an intramolecular Hoesch reaction were unsuccessful, only the corresponding *amide* being produced.


(V.)


(VI.)

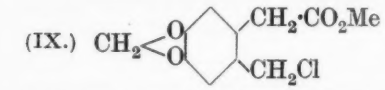
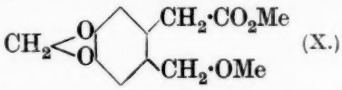
N-Methyl-β-piperonylethylamine is readily monobrominated in the 6-position, as is shown by the preparation of an identical product from 6-bromo-β-piperonylpropionamide (Haworth, Perkin, and Stevens, J., 1926, 1764) by treatment with sodium hypochlorite followed by methylation of the resulting 6-bromo-β-piperonylethylamine. The nitrile (VI) reacts with N-*methyl*-6-*bromo*-β-*piperonylethylamine*, giving N-*methyl*-N-6′-*bromo*-β-*piperonylethyl*-6-*aminomethylhomopiperonylonitrile* (VIII). It was not found possible to close the 10-membered ring, producing the substance (II), by an internal Grignard reaction involving the bromine atom and the nitrile group. As the material was invariably recovered unchanged, and therefore no organomagnesium compound was formed, it did not seem likely that better results would be obtained by preparing the ester corresponding to the nitrile (VIII), and attempting a similar ring-closure.


(VII.)

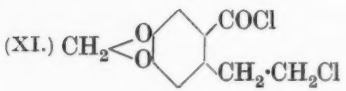
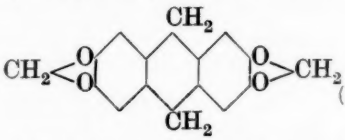

(VIII.)

It was hoped that successive treatment with phosphorus tri-

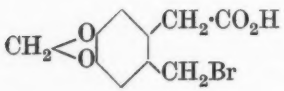
chloride and methyl alcohol would convert the lactone (III) into methyl 6-chloromethylhomopiperonylate (IX), but only the *methoxy*-ester (X) was obtained. This result provides a striking illustration of the mobility of the halogen in the methylenedioxybenzyl halides; the isomeric 6-β-chloroethylpiperonoyl chloride (XI), in which the

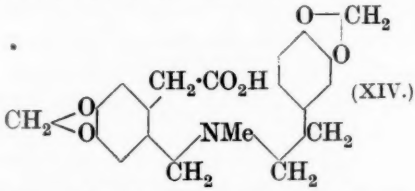
(IX.)   (X.)

halogen is one position farther removed from the benzene nucleus, is smoothly converted into the corresponding chloro-ester (Perkin, J., 1890, **57**, 1032). The methoxyl group in methoxymethylhomopiperonylic acid is removed with remarkable ease: warming with dilute hydrochloric acid on the steam-bath rapidly converts the acid into the lactone (III). In the same way homopiperonyl methyl ether (Greene and Robinson, J., 1922, **121**, 2194) was found to give

(XI.)   (XII.)

2 : 3 : 6 : 7-bismethylenedioxy-9 : 10-dihydroanthracene (XII), which is known to be produced from homopiperonyl alcohol under experimental conditions similar to those employed (compare Ewins, J., 1909, **95**, 1486; G. M. Robinson, J., 1915, **107**, 270).


(XIII.)


(XIV.)

By treatment with hydrogen bromide, the substance (III) is converted into *6-bromomethylhomopiperonylic acid* (XIII), which is reconverted into the lactone by primary or secondary bases but readily forms the *methyl* ester with diazomethane. This ester yields *N-methyl-N-β-piperonylethyl-6-aminomethylhomopiperonylic acid* (XIV) on condensation with *N*-methyl-β-piperonylethylamine and subsequent hydrolysis. It was not found possible to transform this into the compound (II) by conversion into the acid chloride and treatment with aluminium chloride.

Experimental.

Homopiperonylic Acid.—Much of the homopiperonylic acid used in this investigation was prepared by the following method, which

is more convenient and much cheaper than that described by Buck and Perkin (J., 1924, **125**, 1679). Ethyl 3 : 4-methylenedioxymandelate (Barger and Ewins, J., 1909, **95**, 554), when boiled with 5—10% sodium hydroxide solution (10 parts), dissolves at once; the acid is obtained from the cooled and acidified solution: the troublesome hydrolysis with alcoholic alkali described by these authors is unnecessary. The acid (50 g.) is dissolved in acetic acid (500 c.c.) at 50—60°, and dry hydrogen bromide (50 g.) passed in. After 2 hours, the piperonylbromoacetic acid (not isolated) is reduced by addition of zinc dust (50 g.). The mixture is heated for 1½—2 hours on the steam-bath, hydrochloric acid (200 c.c.) added, and, when reaction ceases, the solution is filtered and cautiously diluted with water. Most of the homopiperonylic acid crystallises on standing, and a further quantity is obtained by extraction with chloroform. Yield, 75%.

Lactone of 6-Hydroxymethylhomopiperonylic Acid (III).—Homopiperonylic acid (10 g.), dissolved in hot acetic acid (30 c.c.), is mixed with hydrochloric acid (10 c.c.) and formalin (10 c.c. of 40%) and heated on the steam-bath for 45 minutes. The mixture is poured into water, extracted with chloroform, and the extract concentrated after being washed with sodium bicarbonate solution. The *lactone* separates on cooling and crystallises from alcohol in colourless leaflets, m. p. 137° (Found: C, 62·8; H, 4·2. $C_{10}H_8O_4$ requires C, 62·5; H, 4·2%). It is readily soluble in chloroform, less soluble in alcohol or benzene, very sparingly soluble in hot water, and almost insoluble in light petroleum. Cold sodium carbonate solution has no action on the lactone, but this dissolves readily in warm sodium hydroxide solution, and rapidly separates unchanged in the crystalline condition on acidification.

4 : 5-*Methylenedioxyhomophthalic Acid*.—To a solution of the lactone (2 g.) in warm dilute sodium hydroxide solution kept at 30—40°, potassium permanganate (3 g.), in aqueous solution, is gradually added. The mixture is treated with sulphur dioxide, concentrated, and strongly acidified; the acid then rapidly crystallises. It is freed from any unchanged lactone by solution in sodium carbonate and reprecipitation, and recrystallised from acetic acid, being obtained in small, colourless prisms, m. p. about 240° (decomp.). Perkin and Robinson (*loc. cit.*) give 236° (decomp.) (Found: C, 53·3; H, 3·7. Calc. for $C_{10}H_8O_6$: C, 53·6; H, 3·6%). The isomeric 3 : 4-methylenedioxyhomophthalic acid melts at 203—204° (decomp.) (Haworth, Perkin, and Stevens, *loc. cit.*). More drastic treatment of the lactone with permanganate, in the hope of obtaining hydrastic acid, gave oxalic acid as the only isolable product; further experiments on its oxidation, which are still in progress,

have led, among other results, to the indirect conversion of the lactone (III) into hydrastic acid, thus confirming the constitution assigned to it.

6-*Hydroxymethylhomopiperonylamide* (V).—The lactone (III) (10 g.) is dissolved in hot alcohol (80 c.c.), mixed with ammonia (250 c.c.; *d* 0·880), and warmed on the steam-bath for ½ hour. The solid which separates soon redissolves, and the *amide* (7 g.) crystallises on cooling. It forms fine, white needles from water or alcohol; m. p. 164—167° (Found: C, 57·7; H, 5·5; N, 6·5. $C_{10}H_{11}O_4N$ requires C, 57·4; H, 5·3; N, 6·7%). The substance is readily soluble in hot water or alcohol, very sparingly soluble in chloroform or benzene, and decomposes above its m. p. with evolution of ammonia and regeneration of the original lactone. It is readily hydrolysed by boiling with sodium carbonate solution.

6-*Chloromethylhomopiperonylonitrile* (VI).—Hydroxymethylhomopiperonylamide (10 g.), chloroform (50 c.c.), and phosphorus trichloride (15 c.c.) are boiled for 3 hours. The amide changes to an insoluble syrup, which is slowly converted into a yellow solid. The liquid is decanted cautiously into cold water, and the residue washed with chloroform and dissolved by agitation with successive small quantities of acetone, finally with addition of sodium bicarbonate solution. After filtering, the united liquors are extracted with chloroform, the extract is washed with sodium bicarbonate, dried, and evaporated, and the residue extracted repeatedly with light petroleum. The *nitrile* separates on cooling in long, colourless needles, m. p. 83—85°, which are very soluble in benzene, but rather sparingly soluble in light petroleum (Found: C, 56·9; H, 4·2; Cl, 17·3. $C_{10}H_8O_2NCl$ requires C, 57·3; H, 3·8; Cl, 16·9%).

N-*Methyl*-β-*piperonylethylamine* was prepared by Decker and Becker's method (*Annalen*, 1913, **395**, 335), piperonylidene-β-piperonylethylamine (Decker and Becker, *ibid.*, p. 349), which crystallises more readily and gives a purer product, being used instead of the benzylidene derivative.

N-*Methyl*-N-β-*piperonylethyl*-6-*aminomethylhomopiperonylonitrile* (VII).—The nitrile (VI) (1 g.) is boiled for 12 hours in benzene solution with methyl-β-piperonylethylamine (2·6 g.), and the liquid shaken with dilute hydrochloric acid (10 c.c. of 2*N*), a brown resin forming. The acid layer is separated, the resin and benzene are repeatedly extracted with hot water, and the united washings and acid layer are treated with concentrated hydrochloric acid, which precipitates the hydrochloride of the product as a gum. The liquid (containing the excess of methyl-β-piperonylethylamine) is decanted, the gum decomposed by ammonia, and the base extracted with chloroform and recrystallised from light petroleum. It forms fine,

white needles, m. p. 74—76°, giving a violet solution in warm concentrated sulphuric acid (Found: C, 68·5; H, 5·9; N, 7·9. $C_{20}H_{20}O_4N_2$ requires C, 68·2; H, 5·7; N, 8·0%). The *nitrate* forms minute crystals, m. p. *ca.* 150° with effervescence, which are very sparingly soluble in cold water and almost insoluble in cold dilute nitric acid.

N-*Methyl*-N-β-*piperonylethyl*-6-*aminomethylhomopiperonylamide*.—The base (VII) (0·6 g.) was mixed with dry ether (30 c.c.) and powdered zinc chloride (2·4 g.), stirred, cooled to −20°, and saturated with dry hydrogen chloride. After 12 hours, the mixture was again cooled and saturated with hydrogen chloride, and on the following day it was cautiously poured into water and heated until the ether had evaporated and no more of the gum would dissolve. Ammonia was added, and the base extracted with chloroform and recrystallised from methyl alcohol; it then formed small, white needles, m. p. 140°, very soluble in chloroform or hot methyl alcohol, which gave a violet solution in strong sulphuric acid and were not noticeably attacked by boiling for a short time with strong alkali. Analysis showed it to be the *amide* as stated, not the desired substance (II) [Found: C, 64·8; H, 6·0. $C_{20}H_{22}O_5N_2$ requires C, 64·9; H, 5·9%. $C_{20}H_{19}O_5N$ (II) requires C, 68·0; H, 5·4%]. The same amide is obtained when the substance (VII) is warmed for some time in methyl-alcoholic solution with excess of alkali and 2% hydrogen peroxide. The *picrate* crystallises from methyl alcohol in minute, orange-yellow plates, m. p. 210° (decomp.) after previous softening. Attempts to bring about the intended ring-closure under other conditions, including the use of aluminium chloride as condensing agent, gave no better result.

6-*Bromo*-β-*piperonylethylamine*.—(a) β-Piperonylethylamine hydrochloride is dissolved in water, and a slight excess of bromine, diluted with a little acetic acid, gradually added. The mixture is rendered strongly alkaline, and the oily base is washed by decantation, dissolved in a moderate excess of 2*N*-hydrochloric acid, boiled with charcoal, and concentrated hydrochloric acid added; the hydrochloride of the brominated base soon separates in nearly colourless prisms. The washings from the crude base yield a further small quantity on extraction with benzene, in which the substance is too sparingly soluble for the main portion to be extracted.

(b) 6-Bromo-β-piperonylpropionamide (Haworth, Perkin, and Stevens, *loc. cit.*) (5 g.) is finely powdered and heated to 70° with a solution prepared by passing the chlorine from potassium permanganate (1·2 g.) and excess of hydrochloric acid into aqueous sodium hydroxide (40 c.c. of 10%). After 2 hours, the aqueous layer is decanted, the oil extracted with hot dilute hydrochloric acid,

2. It is found that an equilibrium is established between potassium tolyloxide, water, cresol, and potassium hydroxide; the ester is hydrolysed by the last substance.

3. Constants are calculated which are the product of an equilibrium constant and a velocity coefficient.

4. The equilibrium constant in aqueous solution has been evaluated by two methods.

5. The temperature coefficient has been measured in both aqueous and alcoholic solutions.

6. It is found that esters of strong organic acids react very rapidly as above, and they also slowly form the corresponding *m*-tolyl ether.

7. A new ester, ethyl *m*-tolyloxyacetate, is described.

The author wishes to express his thanks to Dr. Crocker for suggesting the line of the research and for his continued interest therein, and to the London County Council for a grant which has enabled the research to be undertaken.

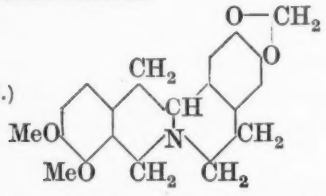
CHELSEA POLYTECHNIC, S.W. [*Received, July 15th*, 1926.]

XXIX.—*Synthetical Experiments on Protopine and Allied Alkaloids. Part I.*

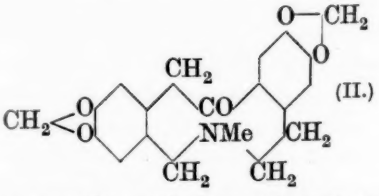
By THOMAS STEVENS STEVENS.

THE present investigation was undertaken with the object of elaborating methods for the production of the ten-membered ring of cryptopine, protopine, and related alkaloids by a direct ring-closure, without previous formation of a structure of the type of tetrahydroberberine (I) (compare Haworth and Perkin, J., 1926, 445, 1769). The synthesis of the isomeride (II) of protopine was first projected, on account of the accessibility of suitable initial materials, and this communication deals with attempts to bring about ring-closure between the carbonyl group and the adjacent benzene nucleus.

(I.)

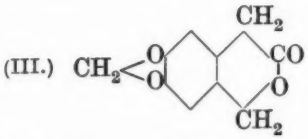


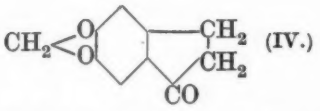
(II.)



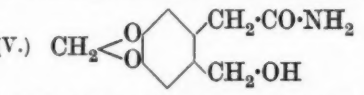
Homopiperonylic acid condenses readily with formaldehyde to give the *lactone* (III) of 6-hydroxymethylhomopiperonylic acid, which was employed as the initial material for the " left-hand half "

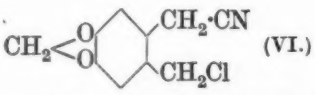
of the molecule (II). The constitution of this lactone was established by oxidation with permanganate, whereby it was converted into the methylenedioxyhomophthalic acid obtained by Perkin and Robinson (J., 1907, **91**, 1086) from 5 : 6-methylenedioxy-1-hydrindone (IV), which latter gives hydrastic acid on oxidation. In the first series of experiments, the lactone was converted by ammonia



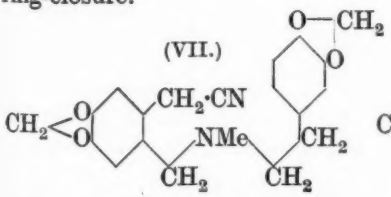


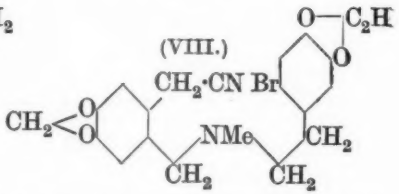
into 6-*hydroxymethylhomopiperonylamide* (V), and the amide treated with phosphorus trichloride, giving 6-*chloromethylhomopiperonylonitrile* (VI). By condensing this nitrile with *N*-methyl-β-piperonylethylamine, N-*methyl*-N-β-*piperonylethyl*-6-*aminomethylhomopiperonylonitrile* (VII) was obtained, but attempts to convert this into (II) by an intramolecular Hoesch reaction were unsuccessful, only the corresponding *amide* being produced.





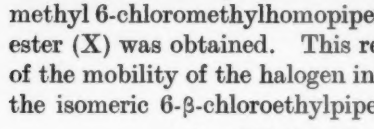
N-Methyl-β-piperonylethylamine is readily monobrominated in the 6-position, as is shown by the preparation of an identical product from 6-bromo-β-piperonylpropionamide (Haworth, Perkin, and Stevens, J., 1926, 1764) by treatment with sodium hypochlorite followed by methylation of the resulting 6-bromo-β-piperonylethylamine. The nitrile (VI) reacts with N-*methyl*-6-*bromo*-β-*piperonylethylamine*, giving N-*methyl*-N-6′-*bromo*-β-*piperonylethyl*-6-*aminomethylhomopiperonylonitrile* (VIII). It was not found possible to close the 10-membered ring, producing the substance (II), by an internal Grignard reaction involving the bromine atom and the nitrile group. As the material was invariably recovered unchanged, and therefore no organomagnesium compound was formed, it did not seem likely that better results would be obtained by preparing the ester corresponding to the nitrile (VIII), and attempting a similar ring-closure.

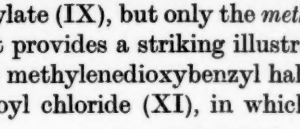




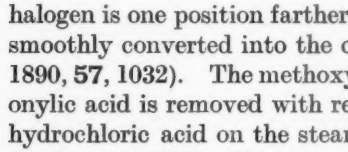
It was hoped that successive treatment with phosphorus tri-

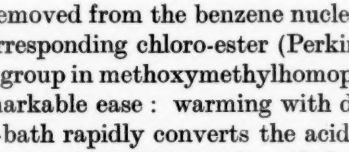
chloride and methyl alcohol would convert the lactone (III) into methyl 6-chloromethylhomopiperonylate (IX), but only the *methoxy*-ester (X) was obtained. This result provides a striking illustration of the mobility of the halogen in the methylenedioxybenzyl halides; the isomeric 6-β-chloroethylpiperonoyl chloride (XI), in which the

(IX.) 

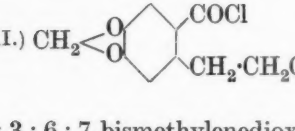
 (X.)

halogen is one position farther removed from the benzene nucleus, is smoothly converted into the corresponding chloro-ester (Perkin, J., 1890, **57**, 1032). The methoxyl group in methoxymethylhomopiperonylic acid is removed with remarkable ease: warming with dilute hydrochloric acid on the steam-bath rapidly converts the acid into the lactone (III). In the same way homopiperonyl methyl ether (Greene and Robinson, J., 1922, **121**, 2194) was found to give

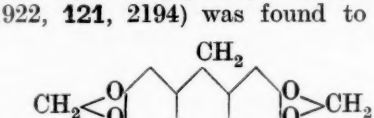
(XI.) 

 (XII.)

2 : 3 : 6 : 7-bismethylenedioxy-9 : 10-dihydroanthracene (XII), which is known to be produced from homopiperonyl alcohol under experimental conditions similar to those employed (compare Ewins, J., 1909, **95**, 1486; G. M. Robinson, J., 1915, **107**, 270).



(XIII.)

 (XIV.)

By treatment with hydrogen bromide, the substance (III) is converted into 6-*bromomethylhomopiperonylic acid* (XIII), which is reconverted into the lactone by primary or secondary bases but readily forms the *methyl* ester with diazomethane. This ester yields N-*methyl*-N-β-*piperonylethyl*-6-*aminomethylhomopiperonylic acid* (XIV) on condensation with *N*-methyl-β-piperonylethylamine and subsequent hydrolysis. It was not found possible to transform this into the compound (II) by conversion into the acid chloride and treatment with aluminium chloride.

EXPERIMENTAL.

Homopiperonylic Acid.—Much of the homopiperonylic acid used in this investigation was prepared by the following method, which

is more convenient and much cheaper than that described by Buck and Perkin (J., 1924, **125**, 1679). Ethyl 3 : 4-methylenedioxymandelate (Barger and Ewins, J., 1909, **95**, 554), when boiled with 5—10% sodium hydroxide solution (10 parts), dissolves at once; the acid is obtained from the cooled and acidified solution: the troublesome hydrolysis with alcoholic alkali described by these authors is unnecessary. The acid (50 g.) is dissolved in acetic acid (500 c.c.) at 50—60°, and dry hydrogen bromide (50 g.) passed in. After 2 hours, the piperonylbromoacetic acid (not isolated) is reduced by addition of zinc dust (50 g.). The mixture is heated for 1½—2 hours on the steam-bath, hydrochloric acid (200 c.c.) added, and, when reaction ceases, the solution is filtered and cautiously diluted with water. Most of the homopiperonylic acid crystallises on standing, and a further quantity is obtained by extraction with chloroform. Yield, 75%.

Lactone of 6-Hydroxymethylhomopiperonylic Acid (III).—Homopiperonylic acid (10 g.), dissolved in hot acetic acid (30 c.c.), is mixed with hydrochloric acid (10 c.c.) and formalin (10 c.c. of 40%) and heated on the steam-bath for 45 minutes. The mixture is poured into water, extracted with chloroform, and the extract concentrated after being washed with sodium bicarbonate solution. The *lactone* separates on cooling and crystallises from alcohol in colourless leaflets, m. p. 137° (Found: C, 62·8; H, 4·2. $C_{10}H_8O_4$ requires C, 62·5; H, 4·2%). It is readily soluble in chloroform, less soluble in alcohol or benzene, very sparingly soluble in hot water, and almost insoluble in light petroleum. Cold sodium carbonate solution has no action on the lactone, but this dissolves readily in warm sodium hydroxide solution, and rapidly separates unchanged in the crystalline condition on acidification.

4 : 5-*Methylenedioxyhomophthalic Acid*.—To a solution of the lactone (2 g.) in warm dilute sodium hydroxide solution kept at 30—40°, potassium permanganate (3 g.), in aqueous solution, is gradually added. The mixture is treated with sulphur dioxide, concentrated, and strongly acidified; the acid then rapidly crystallises. It is freed from any unchanged lactone by solution in sodium carbonate and reprecipitation, and recrystallised from acetic acid, being obtained in small, colourless prisms, m. p. about 240° (decomp.). Perkin and Robinson (*loc. cit.*) give 236° (decomp.) (Found: C, 53·3; H, 3·7. Calc. for $C_{10}H_8O_6$: C, 53·6; H, 3·6%). The isomeric 3 : 4-methylenedioxyhomophthalic acid melts at 203—204° (decomp.) (Haworth, Perkin, and Stevens, *loc. cit.*). More drastic treatment of the lactone with permanganate, in the hope of obtaining hydrastic acid, gave oxalic acid as the only isolable product; further experiments on its oxidation, which are still in progress,

have led, among other results, to the indirect conversion of the lactone (III) into hydrastic acid, thus confirming the constitution assigned to it.

6-*Hydroxymethylhomopiperonylamide* (V).—The lactone (III) (10 g.) is dissolved in hot alcohol (80 c.c.), mixed with ammonia (250 c.c.; *d* 0·880), and warmed on the steam-bath for ½ hour. The solid which separates soon redissolves, and the *amide* (7 g.) crystallises on cooling. It forms fine, white needles from water or alcohol; m. p. 164—167° (Found: C, 57·7; H, 5·5; N, 6·5. $C_{10}H_{11}O_4N$ requires C, 57·4; H, 5·3; N, 6·7%). The substance is readily soluble in hot water or alcohol, very sparingly soluble in chloroform or benzene, and decomposes above its m. p. with evolution of ammonia and regeneration of the original lactone. It is readily hydrolysed by boiling with sodium carbonate solution.

6-*Chloromethylhomopiperonylonitrile* (VI).—Hydroxymethylhomopiperonylamide (10 g.), chloroform (50 c.c.), and phosphorus trichloride (15 c.c.) are boiled for 3 hours. The amide changes to an insoluble syrup, which is slowly converted into a yellow solid. The liquid is decanted cautiously into cold water, and the residue washed with chloroform and dissolved by agitation with successive small quantities of acetone, finally with addition of sodium bicarbonate solution. After filtering, the united liquors are extracted with chloroform, the extract is washed with sodium bicarbonate, dried, and evaporated, and the residue extracted repeatedly with light petroleum. The *nitrile* separates on cooling in long, colourless needles, m. p. 83—85°, which are very soluble in benzene, but rather sparingly soluble in light petroleum (Found: C, 56·9; H, 4·2; Cl, 17·3. $C_{10}H_8O_2NCl$ requires C, 57·3; H, 3·8; Cl, 16·9%).

N-*Methyl*-β-*piperonylethylamine* was prepared by Decker and Becker's method (*Annalen*, 1913, **395**, 335), piperonylidene-β-piperonylethylamine (Decker and Becker, *ibid.*, p. 349), which crystallises more readily and gives a purer product, being used instead of the benzylidene derivative.

N-*Methyl*-N-β-*piperonylethyl*-6-*aminomethylhomopiperonylonitrile* (VII).—The nitrile (VI) (1 g.) is boiled for 12 hours in benzene solution with methyl-β-piperonylethylamine (2·6 g.), and the liquid shaken with dilute hydrochloric acid (10 c.c. of 2*N*), a brown resin forming. The acid layer is separated, the resin and benzene are repeatedly extracted with hot water, and the united washings and acid layer are treated with concentrated hydrochloric acid, which precipitates the hydrochloride of the product as a gum. The liquid (containing the excess of methyl-β-piperonylethylamine) is decanted, the gum decomposed by ammonia, and the base extracted with chloroform and recrystallised from light petroleum. It forms fine,

white needles, m. p. 74—76°, giving a violet solution in warm concentrated sulphuric acid (Found: C, 68·5; H, 5·9; N, 7·9. $C_{20}H_{20}O_4N_2$ requires C, 68·2; H, 5·7; N, 8·0%). The *nitrate* forms minute crystals, m. p. *ca.* 150° with effervescence, which are very sparingly soluble in cold water and almost insoluble in cold dilute nitric acid.

N-*Methyl*-N-β-*piperonylethyl*-6-*aminomethylhomopiperonylamide*.—The base (VII) (0·6 g.) was mixed with dry ether (30 c.c.) and powdered zinc chloride (2·4 g.), stirred, cooled to −20°, and saturated with dry hydrogen chloride. After 12 hours, the mixture was again cooled and saturated with hydrogen chloride, and on the following day it was cautiously poured into water and heated until the ether had evaporated and no more of the gum would dissolve. Ammonia was added, and the base extracted with chloroform and recrystallised from methyl alcohol; it then formed small, white needles, m. p. 140°, very soluble in chloroform or hot methyl alcohol, which gave a violet solution in strong sulphuric acid and were not noticeably attacked by boiling for a short time with strong alkali. Analysis showed it to be the *amide* as stated, not the desired substance (II) [Found: C, 64·8; H, 6·0. $C_{20}H_{22}O_5N_2$ requires C, 64·9; H, 5·9%. $C_{20}H_{19}O_5N$ (II) requires C, 68·0; H, 5·4%]. The same amide is obtained when the substance (VII) is warmed for some time in methyl-alcoholic solution with excess of alkali and 2% hydrogen peroxide. The *picrate* crystallises from methyl alcohol in minute, orange-yellow plates, m. p. 210° (decomp.) after previous softening. Attempts to bring about the intended ring-closure under other conditions, including the use of aluminium chloride as condensing agent, gave no better result.

6-*Bromo*-β-*piperonylethylamine*.—(a) β-Piperonylethylamine hydrochloride is dissolved in water, and a slight excess of bromine, diluted with a little acetic acid, gradually added. The mixture is rendered strongly alkaline, and the oily base is washed by decantation, dissolved in a moderate excess of 2*N*-hydrochloric acid, boiled with charcoal, and concentrated hydrochloric acid added; the hydrochloride of the brominated base soon separates in nearly colourless prisms. The washings from the crude base yield a further small quantity on extraction with benzene, in which the substance is too sparingly soluble for the main portion to be extracted.

(b) 6-Bromo-β-piperonylpropionamide (Haworth, Perkin, and Stevens, *loc. cit.*) (5 g.) is finely powdered and heated to 70° with a solution prepared by passing the chlorine from potassium permanganate (1·2 g.) and excess of hydrochloric acid into aqueous sodium hydroxide (40 c.c. of 10%). After 2 hours, the aqueous layer is decanted, the oil extracted with hot dilute hydrochloric acid,

and the cold filtered solution treated with potassium iodide. The hydriodide which is precipitated, and the benzoyl derivative prepared from it, were shown by mixed m. p. determinations to be identical with those made from the base obtained by process (a); the yield by method (b) is rather poor.

The *hydrochloride* dissolves readily in hot water or alcohol and gives a claret-coloured solution in concentrated sulphuric acid; it melts at 208—210° after sintering and losing its water of crystallisation at 110—120° (Found: C, 36·1; H, 4·3. $C_9H_{10}O_2NBr,HCl,H_2O$ requires C, 36·2; H, 4·4%. 0·1234 gave 0·1382 silver halides. Theory demands 0·1371). The base is a colourless oil, which could not be made to solidify, and absorbs carbon dioxide from the air. The *hydriodide* forms white microcrystals, m. p. 221°, which are fairly easily soluble in water, but much less soluble in potassium iodide solution. The *benzoyl* derivative is prepared in the usual manner and crystallises from methyl alcohol in fine, white needles, m. p. 138—140° (Found: C, 55·4; H, 4·3; Br, 23·3. $C_{16}H_{14}O_3NBr$ requires C, 55·2; H, 4·0; Br, 23·0%).

Piperonylidene-6-bromo-β-piperonylethylamine.—A solution of bromo-β-piperonylethylamine hydrochloride in hot alcohol is rendered just alkaline to phenolphthalein by alcoholic sodium ethoxide and filtered from sodium chloride, a slight excess of piperonal is added, and the mixture boiled for 2 hours. The Schiff's base crystallises on cooling in colourless prisms, m. p. 108—112° (Found: C, 53·9; H, 3·8; N, 3·7. $C_{17}H_{14}O_4NBr$ requires C, 54·3; H, 3·7; N, 3·7%).

N-Methyl-6-bromo-β-piperonylethylamine. — (a) Piperonylidenebromopiperonylethylamine (5 g.) is heated with methyl iodide (3 c.c.) for 5 hours at 100° and the product is dissolved in 90—95% alcohol and boiled for 10 minutes. The hydriodide, which separates on addition of ether, is recrystallised from alcohol–ethyl acetate. In several experiments, apparently carried out under the usual conditions, a considerable quantity of a sparingly soluble salt was obtained, which crystallised from water in white needles, m. p. 260°, behaved like the iodide of a quaternary base, and would appear to be trimethyl-6-bromo-β-piperonylethylammonium iodide (Found: C, 34·6; H, 4·1. $C_{12}H_{17}O_2NBrI$ requires C, 34·8; H, 4·1%). The *picrate* crystallises from alcohol in minute, bright yellow plates, m. p. 151—153°. On boiling the quaternary iodide with 20% potassium hydroxide solution, a volatile oil was formed, presumably *6-bromopiperonylethylene*, but this rapidly polymerised to a plastic resin, insoluble in the ordinary solvents, which was not further investigated.

(b) *N*-Methyl-β-piperonylethylamine is dissolved in 7—10 parts

of dilute hydrochloric acid, treated with the theoretical quantity of bromine diluted with a little acetic acid, and the product precipitated as hydriodide by the addition of a strong solution of potassium iodide.

Methylbromopiperonylethylamine is a colourless oil, readily soluble in benzene. The *hydrochloride* crystallises from alcohol–ether in small, stout needles, m. p. 162—164°, which give a claret-coloured solution in sulphuric acid, turned brown by potassium nitrate. The *hydriodide* forms small, white prisms, m. p. 175°, which dissolve readily in water or alcohol (Found : C, 31·5; H, 3·6. $C_{10}H_{12}O_2NBr,HI$ requires C, 31·1; H, 3·4%). The *benzoyl* derivative, obtained in the usual manner, crystallises from dilute methyl alcohol in clusters of colourless needles, m. p. 98—100° (Found : C, 56·4; H, 4·6. $C_{17}H_{16}O_3NBr$ requires C, 56·4; H, 4·4%).

N-Methyl-N-6′-bromo-β-piperonylethyl-6-aminomethylhomopiperonylonitrile (VIII).—The preparation is similar to that of the halogen-free compound (VII). As the hydrochloride is very sparingly soluble, it is best to evaporate the benzene, dissolve the residue in acetic acid, and pour the solution into hot, very dilute hydrochloric acid (100 c.c.). The mixture is treated with charcoal, and concentrated hydrochloric acid added; the hydrochloride then crystallises, on cooling, in colourless needles, m. p. 205° (Found : C, 51·2; H, 4·3. $C_{20}H_{19}O_4N_2Br,HCl$ requires C, 51·3; H, 4·3%. 0·1154 gave 0·0818 silver halides; theory demands 0·0818). It is sparingly soluble in water or alcohol and gives an emerald-green solution in concentrated sulphuric acid. The *nitrate* separates from dilute nitric acid, in which it is very difficultly soluble, as a microcrystalline powder which decomposes with effervescence at about 160° (Found : Br, 16·2. $C_{20}H_{19}O_4N_2Br,HNO_3$ requires Br, 16·2%).

Repeated attempts were made to bring about an internal Grignard reaction with this substance, but it could not be induced to react with magnesium under any conditions, and the bromine atom was not removed even by prolonged boiling in ligroin with " molecular " potassium.

6-Methoxymethylhomopiperonylic Acid.—(a) The lactone (3 g.) is boiled with chloroform (12 c.c.) and phosphorus trichloride (6 c.c.) for 5 hours, and the mixture is poured into excess of methyl alcohol and warmed on the steam-bath for 2 hours. After dilution with water, the *ester* (X) is extracted with chloroform and distilled in a vacuum; the greater part passes over at 199°/21 mm. as a colourless oil which solidifies in a freezing mixture. It crystallises from dilute methyl alcohol in white needles, m. p. 41—43° (Found : C, 60·2; H, 5·9. $C_{12}H_{14}O_5$ requires C, 60·5; H, 5·9%). The free *acid*, obtained by hydrolysis with methyl-alcoholic potassium hydroxide,

forms colourless needles from benzene–light petroleum, m. p. 93—95°. The *silver* salt is sparingly soluble in hot water (Found : Ag, 32·5. $C_{11}H_{11}O_5Ag$ requires Ag, 32·6%). When the acid is heated with dilute hydrochloric acid (15%) for an hour on the steam-bath, a pink solution is produced which deposits the lactone (III) in an impure condition on cooling.

For purposes of comparison, homopiperonyl methyl ether was mixed with concentrated hydrochloric acid and enough acetic acid to give a homogeneous solution and heated on the steam-bath; crystals soon began to separate, and the ether was finally completely converted into 2 : 3 : 6 : 7-bismethylenedioxydihydroanthracene (XII), which was identified by its insolubility and high m. p., and its conversion, by treatment with nitric acid, into 6 : 6′-dinitro-3 : 4 : 3′ : 4′-bismethylenedioxydiphenylmethane (Ewins, *loc. cit.*; G. M. Robinson, *loc. cit.*), which did not depress the m. p. of an authentic specimen. Both samples of the dinitro-compound crystallised from acetic acid in yellow needles, and not in prisms, as described by Ewins, but gave the correct m. p. (217°).

(b) The methoxy-acid is also formed, along with much of the lactone (III), when bromomethylhomopiperonylic acid (XIII; *vide infra*) is boiled for 2 hours with excess of methyl alcohol, and any ester formed hydrolysed by means of potassium hydroxide.

6-*Bromomethylhomopiperonylic Acid* (XIII).—The lactone (III) is dissolved in a little hot acetic acid, and excess of a strong solution of hydrogen bromide in the same solvent added. After some hours, the white needles that have separated are collected, washed, and recrystallised from benzene. The acid is moderately easily soluble in warm acetic acid, less soluble in benzene or ether, melts at 146—149°, and decomposes at about 180° with evolution of hydrogen bromide (Found : Br, 29·7. $C_{10}H_9O_4Br$ requires Br, 29·3%). On treatment with sodium bicarbonate solution, it is reconverted into the lactone without dissolving completely. Attempts were made to condense the substance with β-piperonylethylamine or its *N*-methyl derivative, but under all conditions tried, even in presence of acetic acid, the lactone (III) was produced : with quinoline, on the other hand, a quaternary salt appeared to be formed, but this was not further investigated. The *methyl* ester is obtained by adding a solution of the acid in warm benzene to excess of diazomethane in well-cooled ether. After several hours, the solvents are evaporated and the residue is extracted several times with light petroleum. The ester separates from the concentrated extract, cooled in ice, and is recrystallised from benzene–light petroleum. It forms hard prisms, m. p. 68—70° with previous softening at about 64°, which are readily soluble in benzene, but sparingly soluble in light petroleum

(Found: Br, 28·1. $C_{11}H_{11}O_4Br$ requires Br, 27·9%). Both bromomethylhomopiperonylic acid and its ester very slowly turn pink on keeping.

N-Methyl-N-β-piperonylethyl-6-aminomethylhomopiperonylic Acid (XIV).—Methyl bromomethylhomopiperonylate (1 mol.), dissolved in benzene, is gradually added to a benzene solution of methyl-β-piperonylethylamine (2 mols.); heat is evolved and a solid rapidly separates. After the benzene has been evaporated, the ester group is hydrolysed by boiling for 1 hour with methyl-alcoholic potassium hydroxide, the liquid diluted, and the excess of methylpiperonylethylamine extracted with benzene. The aqueous layer is acidified, rendered alkaline with ammonia, concentrated, and a solution of oxalic acid added. On standing, the *oxalate* separates and is recrystallised from alcohol–ether and dried at 110°, forming warty aggregates of minute prisms, softening at 173° and melting with effervescence at 178° [Found: C, 60·8; H, 5·6. $(C_{20}H_{21}O_6N)_2,C_2H_2O_4$ requires C, 60·6; H, 5·3%]. Considerable difficulty was experienced in obtaining the free amino-acid in a crystalline condition. The oxalate is dissolved in alcohol, treated with alcoholic ammonia, the ammonium oxalate removed by filtration, and the residue evaporated to dryness and dried in a vacuum. A hard glassy mass remains which slowly crystallises on warming on the steam-bath. In this condition, the substance melts at 136—140°, and is readily soluble in methyl or ethyl alcohol, moderately soluble in chloroform or hot water, and almost insoluble in ether or benzene; it dissolves readily in ammonia, and gives a violet solution in concentrated sulphuric acid. From most of the solvents tried, the amino-acid separates as a gum, but it forms a microcrystalline powder, from chloroform–ether, which contains chloroform of crystallisation (carbylamine reaction), not removed in a steam-oven, and melts to a yellow froth at about 100°. In view of the small quantity available and the intractability of the substance it was not purified for analysis. By the action of thionyl chloride, it was converted into the acid chloride (not isolated), and the latter treated in nitrobenzene solution with aluminium chloride with a view to obtain the compound (II). Considerable decomposition took place, and no pure substance could be isolated in several experiments.

The author's thanks are due to the Ramsay Memorial Trustees for a Fellowship, and to Professor W. H. Perkin for suggesting this investigation and for his kindly interest in its progress.

THE DYSON PERRINS LABORATORY, OXFORD. THE UNIVERSITY, GLASGOW.

[*Received, November 24th*, 1926.]

XXX.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XXXI. The Resolution of* m-*Carboxyphenylmethylsulphine-*p-*toluenesulphonylimine.*

By SYDNEY GEORGE CLARKE, JOSEPH KENYON, and HENRY PHILLIPS.

RAPER discovered that the condensation of chloramine-T with dialkyl sulphides gave rise to compounds of a new type containing a quadrivalent sulphur atom linked to nitrogen. Such compounds were named sulphilimines by Mann and Pope (J., 1922, **121**, 1052), who expressed by the general formula $C_6H_4Me{\cdot}SO_2{\cdot}N{:}SXY$ the constitution of those sulphilimines arising by the use of chloramine-T. These authors (J., 1924, **125**, 911) also pointed out that "the sulphilimines might be expected to exist in enantiomorphously related forms owing to the operation of a trihedral disposition of the three valency directions of the doubly-linked nitrogen atom." It would appear from this statement that they considered that, in a sulphilimine of the above type, the *p*-toluenesulphonyl group was not in the same plane as the groups X and Y, a space arrangement which need not necessarily be similar (as Mann and Pope suggested it should be) to that existing in *cyclo*hexylene dithiocarbonate 2-pyridylhydrazone, which was resolved by Mills and Schindler (J., 1923, **123**, 312). This is true even if the $>S{:}N-$ group of the sulphilimine can produce a similar space arrangement as the $>C{:}N-$ group of the hydrazone. The problem involved was also considered by Mann and Pope to have a bearing on the question whether the four valencies of quadrivalent sulphur are identical or whether one is co-ordinated as was indicated by Werner ("Lehrbuch der Stereochemie," 1904, p. 316).

Mann and Pope prepared and examined *d*- and *l*-camphorylidenemethylethylsulphine-*p*-toluenesulphonylimine

$$(C_{10}H_{14}O{:}CH{\cdot}SEt{:}N{\cdot}SO_2{\cdot}C_6H_4Me)$$

and stated that neither of these compounds furnished any indication of stereoisomerism of the type *d*-C,*d*-S and *d*-C,*l*-S and that therefore they proposed to investigate other methods for realising this type of isomerism.

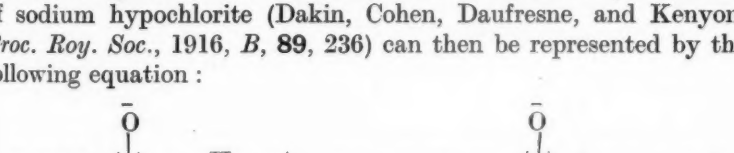
In this communication, however, it is suggested that the sulphilimines contain the group $>\overset{+}{S}\text{–}\overset{-}{N}-$. Any question as to the disposition in space of the three valency directions of the nitrogen atom, which is now linked by two covalencies and one electrovalency, must therefore be left in abeyance. It is nevertheless suggested that

sulphilimines of the type $C_6H_4Me{\cdot}SO_2{\cdot}\overset{-}{N}{\cdot}\overset{+}{S}XY$ should be capable of existing in enantiomorphously-related forms, since the quadrivalent sulphur atoms which they contain are in a state of combination analogous to that of the quadrivalent sulphur atoms of the esters of *p*-toluenesulphinic acid and of mixed sulphoxides the optically active forms of which have been described (Phillips, J., 1925, **127**, 2552; Harrison, Kenyon, and Phillips, J., 1926, 2079). In other words, the positively charged sulphur atom of the sulphilimine molecule can be considered to occupy the apex of a tetrahedron at the other three corners of which lie the groups X and Y and the *p*-toluenesulphonamido-group the nitrogen atom of which bears a negative charge.

To support these suggestions, it is necessary to review the constitution of chloramine-T and its reactions with thio-ethers in the light of the newer electronic theories of valency and the investigations to which those theories have given rise.

The Constitution of Chloramine-T.

Sugden, Reed, and Wilkins (J., 1925, **127**, 1525) have shown, by measurements of the molecular parachors of compounds containing a sexavalent sulphur atom linked to two oxygen atoms (*e.g.*, ethyl ethanesulphonate), that in such compounds the sulphur and oxygen atoms are linked by semipolar double bonds as had been suggested by Lowry (*Trans. Faraday Soc.*, 1923, **18**, 285). Hence the constitution of *p*-toluenesulphonamide, the parent substance of chloramine-T, is doubtless more accurately represented by the formula given in the equation below than by the structural formula by which it is usually indicated. The reaction which occurs when *p*-toluenesulphonamide is converted into chloramine-T by the action of sodium hypochlorite (Dakin, Cohen, Daufresne, and Kenyon, *Proc. Roy. Soc.*, 1916, *B*, **89**, 236) can then be represented by the following equation:

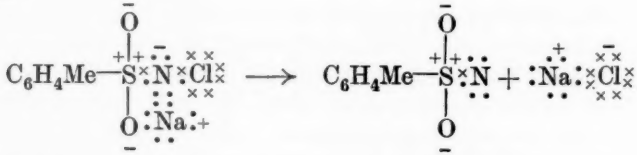


Thus it is suggested that the valencies of the tervalent nitrogen atom which chloramine-T contains are made up of two covalencies and one electrovalency. If, therefore, the sodium ion is considered to be closely attracted to the nitrogen atom, then this atom possesses the same type of tricovalency as that of the nitrogen atom of sodium phthalimide. It should be noticed, however, that the sodium ion

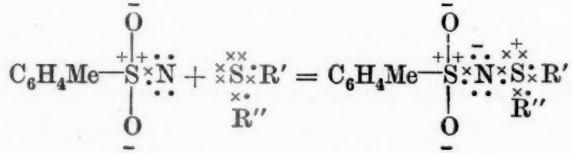
can become attracted to either of the negatively charged sulphoxy-oxygen atoms in the molecule without causing any change in the mode of linking of the nitrogen atom. Hence it would appear that the formulation of chloramine-T as a derivative of *iso*chloramine with the constitution $C_6H_4Me{\cdot}SO(ONa){:}NCl$ (compare Chattaway, J., 1905, **87**, 146, 153; Dakin, Cohen, Daufresne, and Kenyon, *loc. cit.*; Mann and Pope, *loc. cit.*) is not only unnecessary but misleading, since it requires that the sexavalent sulphur atom should be surrounded by twelve valency electrons instead of the normal octet the presence of which around the sulphur atom in such compounds agrees with the experimental results of Sugden, Reed, and Wilkins (*loc. cit.*).

The Condensation of Chloramine-T with Thio-ethers.

The constitutional formula of a sulphilimine is more easily deduced if the condensation of the chloramine-T with the thio-ether is assumed to occur in two stages. Under the experimental conditions employed, during the first stage of the reaction the chloramine-T can be considered to decompose into sodium chloride and an active radical:

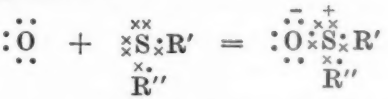


In the above formulæ the electrons represented by crosses in the valency octet of the nitrogen atom are contributed to that octet by the sulphur and chlorine atoms to which the nitrogen atom is united by covalencies. When chloramine-T decomposes as indicated above, it loses the chlorine atom as *an ion* and hence the active radical produced contains a nitrogen atom surrounded by a sextet of valency electrons. It can then be assumed that during the second stage of the condensation this nitrogen atom completes its octet at the expense of one of the two lone pairs of electrons present in the valency shell of the sulphur atom which the thio-ether contains.



These electronic formulæ reveal two points of interest. First, the nitrogen and sulphur atoms cannot become united by a true

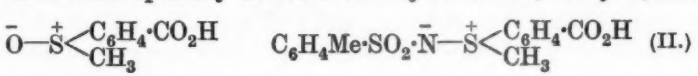
double bond (non-polar double bond), since such a linking would create a surplus of electrons (10 instead of 8) in the valency shells of both atoms. Secondly, the sulphur atom contributes both electrons to form the covalency by which it is subsequently united to the nitrogen atom, and after the union one of these electrons functions as though it had been contributed originally by the nitrogen atom. Hence the nitrogen atom acquires a negative charge (having gained an electron or, alternatively, gained a half share of two electrons), whilst the sulphur atom (having lost an electron, or, alternatively, lost a half share in two electrons) acquires a positive charge. The nitrogen and sulphur atoms thus become united by a semipolar double bond. When viewed from this standpoint, the formation of the sulphilimine becomes strictly analogous to the oxidation of a sulphide to a sulphoxide.



In this instance, the neutral oxygen atom with a sextet of valency electrons completes its octet, as did the nitrogen atom of the *p*-toluenesulphonamido-radical, at the expense of the valency electrons of the sulphur atom.

Resolution of dl-m-*Carboxyphenylmethylsulphine*-p-*toluene-sulphonylimine.*

Since *dl-m*-carboxyphenyl methyl sulphoxide (I) was successfully resolved into its optically active forms by Harrison, Kenyon, and



Phillips (*loc. cit.*), there appeared to be no reason, if the above arguments are valid, why the corresponding sulphilimine (II) should not also be capable of existing in enantiomorphously related forms. dl-m-*Carboxyphenylmethylsulphine*-p-*toluenesulphonylimine* was therefore prepared and examined. It was readily obtained by the condensation of chloramine-T with *m*-carboxyphenyl methyl sulphide. Its *brucine* salt, on recrystallisation from acetone, changed rapidly in rotatory power, and when optically pure the *l*-B, *l*-A salt had $[\alpha]_{5461}$ −144° in ethyl-alcoholic solution. On decomposition of this salt with dilute hydrochloric acid the l-m-*carboxyphenylmethylsulphine*-p-*toluenesulphonylimine* was obtained with $[\alpha]_{5461}$ −338°, $[\alpha]_{4359}$ −627° in ethyl-alcoholic solution. The more soluble brucine salt was recovered from the mother-liquors from the crystallisations of the *l*-B, *l*-A salt, and on decomposition

gave a sulphilimine with $[\alpha]_{5461}$ +145°. This sulphilimine was combined with cinchonidine and the *cinchonidine* salt obtained was repeatedly crystallised from ethyl alcohol until its rotatory power was constant. It then had $[\alpha]_{5461}$ +48·3° in chloroform and on decomposition gave d-m-*carboxyphenylmethylsulphine*-p-*toluenesulphonylimine* with $[\alpha]_{5461}$ +337°, $[\alpha]_{4359}$ +627° in ethyl-alcoholic solution. The satisfactory agreement between the specific rotatory powers of the two enantiomorphs indicates that both were obtained optically pure. The specific rotatory powers of the optically pure sulphilimine in various solvents are in Table I.

TABLE I.

Specific Rotatory Powers of l-m-*Carboxyphenylmethylsulphine*-p-*toluenesulphonylimine in Solvents.*

c = g. of l-sulphilimine in 100 c.c. of solution. $l = 2$. $\alpha_\lambda = 0{\cdot}02c[\alpha]_\lambda$.

Solvents.	c.	λ_{6708}.	λ_{5893}.	λ_{5790}.	λ_{5461}.	λ_{4359}.
Ethyl alcohol	3·0000	209°	276°	293°	338°	627°
Pyridine	3·0000	190	255	265	308	583
Chloroform	0·2505	216	272	288	332	609
Ethyl acetate	0·4146	190	260	267	306	570
Glacial acetic acid ...	2·0000	190	253	266	306	569

This table shows that the specific rotatory power of the optically active sulphilimine is but slightly influenced by solvents. Under the experimental conditions employed, the sulphilimine exhibits complex rotatory dispersion (except possibly when dissolved in ethyl acetate), since curves are obtained when $1/\alpha$ for this compound is plotted against λ^2. Unlike the optically active sulphoxides previously described (Harrison, Kenyon, and Phillips, *loc. cit.*), which differed considerably in physical properties from their racemic modifications, the optically active sulphilimine now described is closely similar to the optically inactive compound. The specific rotatory power of the sulphilimine in solvents remains unchanged on standing, and in this respect it resembles the optically active sulphoxides (*loc. cit.*) rather than the esters of *p*-toluenesulphinic acid (Phillips, *loc. cit.*, p. 2573), which exhibit marked mutarotation in solution.

dl-m-Carboxyphenylmethylsulphine-*p*-toluenesulphonylimine was converted by the action of dilute hydrochloric acid into a mixture of *p*-toluenesulphonamide, *m*-carboxyphenyl methyl sulphide and sulphoxide, whilst the sulphonamide and *m*-carboxyphenylmethylsulphone were the sole products of the action of hydrogen peroxide. Further experiments are under consideration with the object of converting the sulphilimine into an unsymmetrical compound containing sexavalent sulphur.

EXPERIMENTAL.

dl-m-*Carboxyphenylmethylsulphine*-p-*toluenesulphonylimine*.—To a solution of *m*-methylthiolbenzoic acid (100 g.) in warm alcohol (500 c.c.) made just alkaline by the addition of 3*N*-sodium hydroxide, chloramine-T (190 g.; 1·1 mols.) in warm water (550 c.c.) was added, and the mixture heated on a steam-bath for 2 hours. Dilute hydrochloric acid was added to the resulting solution after cooling and dl-m-*carboxyphenylmethylsulphine*-p-*toluenesulphonylimine* then separated, m. p. 160—164°. Yield 150 g. (75%). By recrystallisation from aqueous ethyl alcohol it was obtained as small needles, m. p. 173—175° (Found: C, 53·6; H, 4·5; N, 4·2. $C_{15}H_{15}O_4NS_2$ requires C, 53·4; H, 4·5; N, 4·2%. 0·3370 required 0·0404 of sodium hydroxide; theory requires 0·0400).

Resolution of dl-m-*Carboxyphenylmethylsulphine*-p-*toluenesulphonylimine*.—(a) *By means of brucine.* To *dl-m*-carboxyphenylmethylsulphine-*p*-toluenesulphonylimine (105 g.) in acetone (500 c.c.), brucine (124 g.) was added, and the mixture was warmed until solution was complete. After cooling, the brucine salt (m. p. 95—105°) which crystallised was removed and recrystallised from four successive quantities (about 1000 c.c. in each case) of acetone until constancy of rotatory power was reached.

l-*Brucine* l-m-*carboxyphenylmethylsulphine*-p-*toluenesulphonylimine* had m. p. 123—125°, $[\alpha]_{5461}$ −144°, $[\alpha]_{4359}$ −279° in ethyl alcohol ($l = 2$; $c = 2{\cdot}500$).

The optically pure salt, dissolved in warm ethyl alcohol, was added to dilute hydrochloric acid. After 48 hours, the l-m-*carboxyphenylmethylsulphine*-p-*toluenesulphonylimine* had separated completely. It crystallised from aqueous ethyl alcohol in prismatic needles, m. p. 172—173°. Its specific rotatory power in various solvents is recorded in Table I.

(b) *By means of cinchonidine.* The acetone mother-liquor from the first crystallisation of the brucine salt described above was added to dilute hydrochloric acid. The *d* + *dl-m*-carboxyphenylmethylsulphine-*p*-toluenesulphonylimine (18·5 g.; with $[\alpha]_{5461}$ +145°) which was precipitated was dissolved in ethyl alcohol (70 c.c.) and to the warm solution cinchonidine was added (16·1 g.). After standing over-night, the cinchonidine salt, m. p. 193—194°, was removed by filtration and repeatedly crystallised from the minimum of ethyl alcohol (about 200 c.c.) until its rotatory power remained unchanged. The l-*cinchonidine* d-m-*carboxyphenylmethylsulphine*-p-*toluenesulphonylimine* thus obtained had m. p. 204°, and $[\alpha]_{6708}^{17\cdot5^\circ}$ +29·42°, $[\alpha]_{5893}^{17\cdot5^\circ}$ +38·47°, $[\alpha]_{5780}^{17\cdot5^\circ}$ +46·76°, $[\alpha]_{5461}^{17\cdot5^\circ}$ + 48·27°, $[\alpha]_{4359}^{17\cdot5^\circ}$ + 102·6°, in chloroform solution ($c = 1{\cdot}326$, $l = 2{\cdot}0$). On decomposition, as previously described, it gave d-*carboxyphenyl-*

methylsulphine-p-*toluenesulphonylimine*, m. p. 172—173°, $[\alpha]_{5461}$ + 337°, $[\alpha]_{4359}$ +627° in ethyl alcohol ($c = 2{\cdot}59$, $l = 1{\cdot}0$).

The Interaction of dl-m-*Carboxyphenylmethylsulphine*-p-*toluenesulphonylimine and Hydrochloric Acid.*—A clear deep red solution was obtained by heating the *dl*-sulphilimine (6·74 g.) with concentrated hydrochloric acid (18 c.c.) on a steam-bath for 5 minutes. From the solution, neutralised by means of sodium carbonate, *p*-toluenesulphonamide (1·62 g.), m. p. 137°, was precipitated, whilst the products which remained dissolved consisted of two acids which were obtained after acidification of the concentrated solution, and were separated by fractional crystallisation from aqueous ethyl alcohol into *m*-carboxyphenyl methyl sulphoxide (1·4 g.), m. p. 171°, and *m*-methylthiolbenzoic acid (1·45 g.), m. p. 127—128°. The overall yield of hydrolytic products was therefore 66%.

The Interaction of dl-m-*Carboxyphenylmethylsulphine*-p-*toluenesulphonylimine and Hydrogen Peroxide.*—A mixture of the sulphilimine (2 g.) and perhydrol (20 c.c.) was heated on a steam-bath with occasional shaking; a clear solution resulted after 15 minutes. The crystalline material (1·6 g.), m. p. 130—180°, which separated on cooling, was crystallised from a small bulk of ethyl alcohol, glistening leaflets (0·7 g.) of *m*-carboxyphenylmethylsulphone (m. p. 229—230° either alone or mixed with an authentic specimen) being obtained. After dilution, the filtrate yielded a second crop of crystals (0·9 g.) which proved to be *p*-toluenesulphonamide, m. p. 135—136°. The original hydrogen peroxide filtrate was evaporated to small bulk; a further quantity (0·29 g.) of *m*-carboxyphenylmethylsulphone was then obtained.

BATTERSEA POLYTECHNIC,
LONDON, S.W. 11.

[*Received, December 7th*, 1926.]

XXXI.—*Studies in the Penthian* Series. Part I. The Action of Sodium Ethoxide on Ethyl β-Thiodipropionate.*

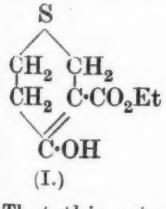
By GEORGE MACDONALD BENNETT and LESLIE VIVIAN DONALD SCORAH.

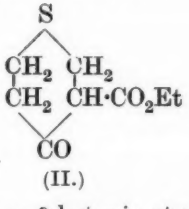
THE researches of V. Meyer and his students led to the isolation of 3-methylpenthiophen (3-methyl-$\Delta^{2:5}$-penthiadiene) in very poor yield from the products of distillation of α-methylglutaric acid with phosphorus trisulphide (Krekeler, *Ber.*, 1886, **19**, 3266), but very

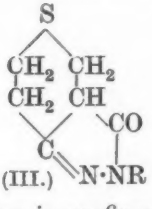
* In order to simplify the nomenclature of this group, we propose, after consultation with the Editor, to name the parent substance (tetrahydropenthiophen or pentamethylene sulphide) *penthian*.

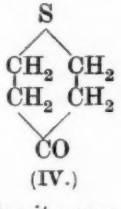
little has since been added to our knowledge of the chemistry of compounds containing this ring system. Penthian itself (v. Braun and Trümpler, *Ber.*, 1910, **43**, 547; Clarke, J., 1912, **101**, 1805) and its 2-methyl derivative (Grischkevitsch-Trochimovski, *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 928) have been prepared by the closure of the ring by the action of sodium sulphide on the αε-dihalogenated paraffin, whilst Apitzsch (*Ber.*, 1904, **37**, 1599; 1905, **38**, 2888; 1908, **41**, 4028; 1909, **42**, 2940) has shown that the products of condensation of carbon disulphide and ketones are derived from penthiadien-4-one.

Simple substituted derivatives of penthian have not hitherto been prepared by smooth ring-closure from open-chain compounds. V. Meyer suggested (*Ber.*, 1886, **19**, 3260) the application of the malonic ester method to ββ′-dichlorodiethyl sulphide for this purpose, but this reaction has recently been shown by Davies (J., 1920, **117**, 297) to yield under various conditions, not the desired penthiandicarboxylic ester, but solely the open-chain tetracarboxylic ester, $S[CH_2{\cdot}CH_2{\cdot}CH(CO_2Et)_2]_2$. We have now subjected ethyl β-thiodipropionate, $S(CH_2{\cdot}CH_2{\cdot}CO_2Et)_2$, to the Dieckmann reaction: the reaction proceeds readily in presence of sodium ethoxide or sodamide to yield the oily enolic ester (I), *ethyl* Δ^3*-penthien-4-ol-3-carboxylate*, which gives an intense purple coloration with ferric chloride. This ester, on keeping, ultimately deposits long needles of the ketonic ester (II), *ethyl penthian-4-one-3-carboxylate*, which gives a delayed reaction with ferric chloride and dissolves only slowly in aqueous solutions of sodium hydroxide.


(I.)


(II.)


(III.)


(IV.)

That this ester has a β-ketonic structure is confirmed by its condensation with hydrazines to yield pyrazolones of the general formula (III), and by its hydrolysis by cold dilute alkali or hot dilute acid to give a crystalline ketone, *penthian-4-one* (IV), readily volatile in steam. Penthianone furnishes, not only the usual derivatives of a cyclic ketone, such as the *oxime*, the *semicarbazone*, the *dinitrophenylhydrazone* and the *dibenzylidene* derivative, but also others due to the reactivity of the sulphur atom, namely, a crystalline *sulphonium methiodide* and a *platinic chloride* compound of the composition $2C_5H_8OS,PtCl_4$.

The yield of cyclic ester (43%) obtained in this investigation was

consistently lower than that (60%) in the analogous reaction with ethyl pimelate carried out by Dieckmann (*Annalen*, 1901, **317**, 93). This raises the question whether the substitution of a sulphur atom for a methylene group in a chain diminishes the tendency to ring closure.

As far as we are aware, these experiments constitute the first instance of the closure of a simple heterocyclic ring by means of the Dieckmann reaction. The method should be applicable in a similar manner to analogous substances where sulphur is replaced by oxygen, nitrogen, or other element.

Experimental.

Preparation of β-Thiodipropionic Acid and its Derivatives.—The preparation described by Loven (*Ber.*, 1896, **29**, 1136) was modified as follows : To a solution of potassium hydroxide (23·5 g.) and sodium sulphide (72 g. of $Na_2S,9H_2O$) in water (190 c.c.), β-iodopropionic acid (100 g.) was added and the mixture was boiled for 15 minutes, cooled to — 10°, and acidified with concentrated hydrochloric acid (50 c.c.). The acid, filtered off after a few hours and washed with a little water, was practically pure (yield 70%). It may be recrystallised from hot water or xylene. It was more economically obtained and in slightly better yield by substituting β-bromopropionic acid (77 g.) for the iodo-acid in the above preparation, and boiling the mixture for 1 hour. A further addition to the yield is obtained by extracting the mother-liquor with ether.

Thiodipropiondiamide, prepared by the action of concentrated aqueous ammonia on the ester (see below) or on the acid chloride obtained from thiodipropionic acid by the action of thionyl chloride, crystallised from ethyl alcohol in colourless plates, m. p. 177—178·5° (Found : N, 15·6; S, 18·2. $C_6H_{12}O_2N_2S$ requires N, 15·9; S, 18·2%).* *Thiodipropiondianilide*, prepared from the acid and boiling aniline in the usual manner, separated from toluene in colourless scales, m. p. 163·5° (Found : N, 8·5; S, 9·8. $C_{18}H_{20}O_2N_2S$ requires N, 8·5; S, 9·8%).

Ethyl thiodipropionate was obtained as a pale straw-coloured oil, b. p. 174°/15 mm. (yield 70% by the Fischer and Speier method; 90% by the continuous process as in " Organic Syntheses," **1**, 68). It has a strong, unpleasant odour, and does not solidify at — 20° (Found : S, 13·8, 13·6; equiv. by saponification, 117·4. $C_{10}H_{18}O_4S$ requires S, 13·7%; equiv., 117·1). The following constants were determined : $d_{4^\circ}^{20^\circ}$ (vac.) 1·1034, $n_\alpha^{20^\circ}$ 1·46938, $n_\beta^{20^\circ}$ 1·47911, whence $[R_L]_\alpha$ 59·17 (calc., 59·30) and $[R_L]_\beta$ 60·20 (calc., 60·29).

* Determinations of sulphur were made by the method of Leonard (*J. Amer. Chem. Soc.*, 1923, **45**, 255).

Ethyl Penthian-4-one-3-carboxylate. — Preliminary experiments showed that ethyl thiodipropionate, subjected to the action of sodium metal in boiling toluene (Bouveault, *Bull. Soc. chim.*, 1899, **21**, 1019), suffered profound decomposition with production of much sodium sulphide. It was found best to use sodium ethoxide at a low temperature in the following manner: To sodium ethoxide, made from Brühl sodium (8 g.) in a flask fitted with a stirrer and a reflux condenser, a solution of ethyl thiodipropionate (40 g.) in dry ether (150 c.c.) was carefully added. The mixture, cooled in a freezing mixture, was stirred for 6 hours, allowed to rise to the ordinary temperature over-night, and then poured into a mixture of ice and acetic acid (22 g.). The lower aqueous layer was removed and extracted twice with ether and the extracts were added to the original ethereal layer. The ethereal solution was then shaken seven times with diminishing amounts of 5% potassium hydroxide solution (530 c.c. in all), the alkaline solution in each case being immediately run into a mixture of ice and acetic acid. The oil thus precipitated was collected in carbon tetrachloride and the extract was shaken twice with *N*/2-sodium carbonate (100 c.c.) to remove the acid ester which was present, and distilled. *Ethyl* Δ^3*-penthien-4-ol-3-carboxylate* (I) (14 g.; 43% yield) was thus obtained as an almost colourless oil of characteristic odour, b. p. 150—151°/16 mm. (Found: C, 50·7; H, 6·5; S, 17·3. $C_8H_{12}O_3S$ requires C, 51·0; H, 6·4; S, 17·0%). This ester gives an immediate purple coloration with alcoholic ferric chloride and dissolves at once in aqueous sodium hydroxide. The residual ethereal solution in the above preparation yielded ethyl thiodipropionate (4 g.) on distillation. A slightly higher yield of the cyclic ester was obtained when sodamide (2 mols.) was used in place of sodium ethoxide. The following constants were determined with a freshly-prepared specimen of the ester which had been twice redistilled, the initial and the final fractions being rejected: $d_4^{20°}$ (vac.) 1·2011, $n_\alpha^{20°}$ 1·51574, $n_\beta^{20°}$ 1·52938, whence $[R_L]_\alpha$ 47·29 (calc., 47·35) and $[R_L]_\beta$ 48·34 (calc., 48·33).*

When this enolic ester had been kept for about a week, it began to deposit crystals of its ketonic tautomeric form, *ethyl penthian-*

* The values in brackets have been calculated using the constants for sulphides found by Price and Twiss (J., 1912, **101**, 1259). No allowance was made for ring-closure, this being justified by the value for penthian itself found by Clarke (*ibid.*, 1800): $[R_L]_\alpha$ 30·61 (calc., 30·84). The values calculated for the ketonic form of the ester would have been 46·21 and 47·20, respectively. It must be admitted that the agreement obtained above may be in part fortuitous, since an exaltation due to conjugation is to be expected in an enolic form: moreover, it is probable that the enolic ester examined already contained some of the ketonic form.

4-*one*-3-*carboxylate* (II), which was dried on porous earthenware and obtained as colourless needles having a high double refraction and an oblique extinction, being probably monoclinic; m. p. 59° (Found : C, 51·05; H, 6·0. $C_8H_{12}O_3S$ requires C, 51·0; H, 6·4%).

This substance differs from the enolic ester in that it dissolves only slowly in aqueous sodium hydroxide and gives no immediate coloration with ferric chloride, the purple colour appearing and increasing in intensity for several minutes. The coloration is not destroyed by the addition of dilute acetic acid. Concentrated aqueous barium hydroxide acts on either of the esters to produce a sparingly soluble, pale yellow *barium* salt. No crystalline copper salt could be obtained.

Pyrazolone Derivatives (III).—The freshly-distilled enolic ester (2 g.) condensed with phenylhydrazine (1·19 g.) on being heated with it and two drops of acetic acid at 100° for 2 hours. The *phenylpyrazolone* crystallised from methyl alcohol in cream-coloured needles, m. p. 219° (Found : N, 12·1. $C_{12}H_{12}ON_2S$ requires N, 12·1%). The reactions between the ester and *p*-bromo- and *p*-nitrophenylhydrazine were carried out in ethyl-alcoholic solution, equimolecular quantities being heated at its boiling point in presence of a few drops of acetic acid for 4 hours. The p-*bromophenylpyrazolone* crystallises from glacial acetic acid in almost colourless plates, m. p. 221·5° (Found : N, 8·7; Br, 25·8. $C_{12}H_{11}ON_2BrS$ requires N, 9·0; Br, 25·7%). The p-*nitrophenylpyrazolone* forms buff-coloured plates from alcohol; m. p. 210·5° (Found : N, 15·1. $C_{12}H_{11}O_3N_3S$ requires N, 15·2%).

Hydrolysis of the Cyclic Ester to yield Penthian-4-*one*.—The cyclic ester (5 g.) was kept for 3 days at the ordinary temperature with 5% potassium hydroxide solution (60 c.c.), the mixture was then extracted with ether, and the ether evaporated. The residue (1·5 g.), which crystallised at once, was *penthian*-4-*one* (IV). This substance separates from petroleum (b. p. 40—60°) in tufts of colourless plates, m. p. 65—66° (Found : C, 51·7; H, 6·9. C_5H_8OS requires C, 51·7; H, 6·9%). The crystals are biaxial with a straight extinction, being probably monoclinic; an optic axis is visible in convergent polarised light and the double refraction is exceptionally high. The substance is appreciably volatile at the ordinary temperature and readily so in steam. It has a strong, characteristic odour and is readily soluble in all the usual organic solvents, slightly less soluble in light petroleum, and moderately easily soluble in cold water.

Preliminary experiments had shown the hydrolysis of the cyclic ester by means of barium hydroxide solution to be very slow and incomplete, probably owing to the sparing solubility of the barium

salt which was at once precipitated. On the other hand, acid hydrolysis was very effective; the ester (1·2 g.) was boiled with 10% sulphuric acid (10 c.c.) for 4 hours; the solution then deposited some of the ketone in a crystalline condition on cooling. Extraction with ether and crystallisation of the residue from light petroleum gave the pure ketone (0·64 g.; 85% yield).

Direct Preparation of Penthianone from Ethyl Thiodipropionate.—The ketone is most conveniently prepared by allowing ethyl thiodipropionate (40 g.) to react with sodium ethoxide (from 8 g. of sodium) as previously described, pouring the reaction mixture into water, removing the upper ethereal layer and extracting it three times with potassium hydroxide solution (5% : 300 c.c.), and keeping the combined alkaline aqueous solutions for 3 days; extraction with ether then yields the ketone (6·7 g.; 33% yield).

Derivatives of Penthianone.—The *oxime*, prepared in aqueous solution and isolated by extraction with ether, is readily soluble in most solvents. It crystallises from warm water, in which it is easily soluble, in colourless, flat needles, m. p. 84—85° (Found : N, 10·7. C_5H_9ONS requires N, 10·7%). The *semicarbazone*, prepared by means of semicarbazide acetate, was crystallised once from toluene, in which it is sparingly soluble, and once from ethyl acetate, in which it is readily soluble, as silvery plates, m. p. 151° (Found : N, 24·2. $C_6H_{11}ON_3S$ requires N, 24·3%). The 2 : 4-*dinitrophenylhydrazone* was precipitated at once on mixing the ketone and the hydrazine (1 mol.) in glacial acetic acid solution; it crystallised from this solvent, in which it is very sparingly soluble, in orange plates, m. p. 186° (Found : N, 18·9. $C_{11}H_{12}O_4N_4S$ requires N, 18·9%).

To a solution of the ketone (0·15 g.) and benzaldehyde (0·35 g.) in ethyl alcohol (2 c.c.), 25% potassium hydroxide solution (10 drops) was added. After a short time, the mixture became a paste of crystals of *dibenzylidenepenthianone*. The substance was crystallised once from ethyl alcohol and once from petroleum (b. p. 90—120°), from which it separated in yellow, compact tufts of crystals, m. p. 149—151° (Found : C, 77·8; H, 5·6. $C_{19}H_{16}OS$ requires C, 78·0; H, 5·5%).

The *dipiperonylidene* derivative, prepared in a precisely similar manner, crystallised from ethyl acetate in yellow tufts of pointed needles, m. p. 181°. It is more soluble in the common solvents than is the benzylidene derivative.

A *compound* with platinic chloride was obtained as a microcrystalline powder by mixing the components in dilute methylalcoholic solution, the precipitate appearing after the mixture had remained for a short time at the ordinary temperature. It was

collected, washed with a little water, and dried in a desiccator. It is easily soluble in epichlorohydrin, from which it crystallises in small, yellow polyhedra which decompose on heating without melting (Found : Pt, 35·2. $C_{10}H_{16}O_2Cl_4S_2Pt$ requires Pt, 34·3%).

The ketone combined slowly with methyl iodide in cold benzene solution, but much more rapidly in the absence of a solvent, a solution of the ketone in an excess of methyl iodide depositing a mass of crystals in the course of a few days. The *penthianone-methylsulphonium iodide* thus obtained was insoluble in benzene, acetone or absolute ethyl alcohol, very soluble in water, and separated from 96% alcohol in pale yellow crystals, m. p. 112—113° (with effervescence due to dissociation) (Found : I, 48·9. $C_6H_{11}OIS$ requires I, 49·2%). An aqueous solution of this salt was digested with an excess of freshly-precipitated silver chloride and the resulting solution of the corresponding chloride was mixed with an excess of platinic chloride, but no chloroplatinate separated from solution even after long keeping. This chloroplatinate must therefore be unusually soluble in water.

Our thanks are due to the Chemical Society for a grant which has defrayed most of the expense of this investigation.

THE UNIVERSITY, SHEFFIELD. [*Received, November 30th*, 1926.]

XXXII.—*The Mechanism of the Formation of Citric and Oxalic Acids from Sugars by* Aspergillus Niger. *Part I.*

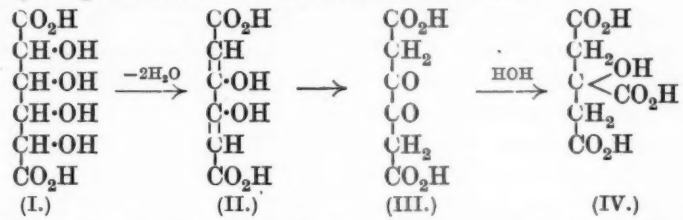
By FREDERICK CHALLENGER, VIRA SUBRAMANIAM, and THOMAS KENNEDY WALKER.

THE production of citric and oxalic acids during the growth of *Aspergillus niger* and similar organisms on glucose or sucrose was first demonstrated by Wehmer (*Bot. Ztg.*, 1891, **49**, 233; *Bull. Soc. chim.*, 1893, **9**, 728; *Ber.*, 1924, **57**, 1659) and has formed the subject of various patent specifications (D.R.-PP. 72957, 91891). This transformation was further investigated by Currie (*J. Biol. Chem.*, 1917, **31**, 33) and by Butkewitsch (*Biochem. Z.*, 1923, **136**, 225; **142**, 195; 1924, **145**, 458).

Molliard (*Compt. rend.*, 1922, **174**, 881; 1924, **178**, 41, 161), Bernhauer (*Biochem. Z.*, 1924, **153**, 517; 1926, **172**, 296), and Butkewitsch (*ibid.*, 1924, **154**, 177) detected gluconic acid at an early stage of the fermentation, but were unable to convert this acid into citric acid under the conditions of their experiments. This has recently been accomplished by Wehmer (*Ber.*, 1925, **58**, 2616)

and by Schreyer (*ibid.*, 2647). Gluconic acid appears to be the first step in the conversion of sugar into citric acid, although some difference of opinion has existed upon this point (Molliard, *loc. cit.*; Falck and Kapur, *Ber.*, 1924, **57**, 920).

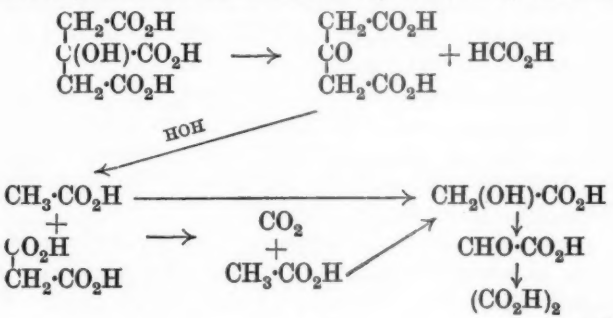
Franzen and Schmitt (*Ber.*, 1925, **58**, 222) have shown that βγ-diketoadipic acid (III) undergoes a " benzilic acid transformation " in presence of alkali-metal hydroxide, yielding citric acid (IV), and suggested that the biological formation of this acid proceeds in an analogous manner, the diketo-acid being supposed to arise from saccharic acid (I), although the production of this acid from sugar by mycological action had not been demonstrated :



(I.) (II.) (III.) (IV.)

Two of the present authors have commenced a comprehensive investigation of the production of organic acids by *A. niger*, and the present communication describes results which have been obtained from a study of the conversion of citric into oxalic acid by the mould. This stage of the oxalic fermentation has received little attention from previous workers with the exception of Raistrick and Clark (*Biochem. J.*, 1919, **13**, 329), who examined the action of *A. niger* on various possible intermediate products.

In an endeavour to discover the mechanism of this process, a hypothesis was formulated which, from purely chemical considerations, might be regarded as a possible explanation. A search has been made in various cultures for some of the intermediate products thus suggested, and conversely the behaviour of these compounds to the mould has been studied. The tentative explanation of the decomposition of citric acid is represented by the scheme :



Raistrick and Clark (*loc. cit.*) found scarcely any oxalic acid when the mould was grown upon malonic, glyoxylic, or glycollic acid. The possibility of a conversion of malonic acid into carbon dioxide by way of mesoxalic and glyoxylic acids is not excluded :

$$\begin{matrix} CO_2H \\ | \\ CH_2 \\ | \\ CO_2H \end{matrix} \longrightarrow \begin{matrix} CO_2H \\ | \\ CO \\ | \\ CO_2H \end{matrix} \longrightarrow \begin{matrix} CO_2 \\ + \\ CHO \\ | \\ CO_2H \end{matrix} \longrightarrow H_2O + 2CO_2.$$

The culture medium used throughout the present research was that of Molliard (*Compt. rend.*, 1919, **168**, 360), in which the amount of inorganic salts is the minimum. The sugar was entirely replaced by citric or other organic acid. The *Aspergillus* strain was kindly supplied by Professor Carl Neuberg, of Berlin–Dahlem, and the solutions were incubated at 30—32°.

In three separate experiments, the formation of glyoxylic acid was observed after 15, 17, and 18 days, respectively. This was first detected by the reddish-violet colour produced with hydrochloric acid and naphtharesorcinol (1 : 3-dihydroxynaphthalene, Neuberg, *Biochem. Z.*, 1910, **24**, **436**) and afterwards as the aminoguanidine derivative (Döbner and Gärtner, *Annalen*, 1901, **315**, 8; **317**, 157). Glyoxylic acid was also obtained by the action of *A. niger* on solutions containing only malonic acid and the inorganic salts of the medium. It was characterised as before.

It does not necessarily follow, although it is very probable, that glyoxylic acid is a stage in the citric ⟶ oxalic change. The quantities of the aminoguanidine derivative so far obtained are too small to warrant definite conclusions on this point. They were, however, precipitated in very dilute solution. Dakin (*J. Biol. Chem.*, 1906, **1**, 271) states that glyoxylic acid is frequently detected in cultures of moulds and bacteria, but gives no details. He also found traces of this acid in sterilised media containing glycine or creatinine. The possibility that the aminoguanidine derivative might arise from traces of glyoxylic acid in the glacial acetic acid employed by us has been excluded by blank experiments and the use of pure acetic acid.

Cultures of the mould on citric acid were next examined for the presence of malonic acid, and this was detected in several experiments by addition of benzenediazonium chloride and sodium acetate, hydrogen formazyl, $CH(N_2Ph){:}N{\cdot}NHPh$ (von Pechmann, *Ber.*, 1892, **25**, 3175), being obtained.

The production of this compound from glyoxylic acid phenylhydrazone and benzenediazonium chloride has also been observed (Busch and others, *Ber.*, 1925, **58**, 442; 1926, **59**, 1162). Its form-

ation in our experiments could not be due to the glyoxylic acid, since this cannot give a hydrazone with benzenediazonium chloride, and the reduction of the latter to phenylhydrazine appears most unlikely. No hydrogen formazyl was produced when the diazonium salt was added to mixtures of glyoxylic acid and the inorganic salts of the medium. Further, in no case during these experiments have we been able to detect the presence of glyoxylic acid before the formation of malonic acid.

The presence of malonic acid in the citric acid cultures has, however, been confirmed in a most satisfactory manner (*a*) by the method of Bougault (*J. Pharm. Chim.*, 1913, **8**, 289; *Ann. chim. anal.*, 1918, **23**, 154), cinnamylidenemalonic acid being isolated, and (*b*) by isolation of the free acid from its lead salt obtained from the evaporated culture.

Many attempts to detect acetonedicarboxylic acid in the citric acid cultures by the use of benzenediazonium chloride, with which it reacts readily (von Pechmann and Jenisch, *Ber.*, 1891, **24**, 3257; Henle and Schapp, *Ber.*, 1905, **38**, 1372), were unsuccessful. In one experiment, a reddish-purple coloration was produced on addition of ferric chloride.

Nevertheless, the transient formation of this acid seems indicated by the fact that on about the seventh or eighth day, *i.e.*, in the early stages of the fermentation, the citric acid–Molliard medium, although giving no ferric chloride reaction, contains acetone. The iodoform reaction, a red colour with alkaline sodium nitroprusside, and a white precipitate with acidified mercuric sulphate (Denigès's solution, *Ann. Chim. phys.*, 1899, **18**, 384) are obtained. Denigès (*loc. cit.*) gives the composition of the wet precipitate as $6HgSO_4,9HgO,4C_3H_6O$. This was decomposed with sodium iodide (Biilmann, *Ber.*, 1902, **35**, 2584), and the acetone characterised as the dibenzylidene derivative and as the *p*-nitrophenylhydrazone.

This appears to be the first recorded instance of the production of acetone by a mould, the well-known fermentation processes for its manufacture (Fernbach and Strange, E.P. 1912, 21073; Gill, *J. Soc. Chem. Ind.*, 1919, **38**, 273T; Speakman, *ibid.*, 155T; *J. Biol. Chem.*, 1920, **41**, 319) depending on the use of bacteria. The authors hope shortly to describe the results of some large-scale experiments. Owing to our failure to detect acetonedicarboxylic acid, it appeared possible that the acetone might arise from acetic acid. It should be mentioned, however, that, apart from an unconfirmed observation recorded by Heinze (*Annales mycologici*, 1903, **1**, 350), acetic acid has not been found in *Aspergillus niger* cultures on sugar or citric acid. Reilly, Hickinbottom, Henley, and Thaysen (*Biochem. J.*, 1920, **14**, 229) and Bakonyi (*Biochem. Z.*, 1926, **169**,

125) have shown that addition of acetic acid to the cultures increases the yield of acetone in the technical fermentation processes.

When grown on a solution of calcium acetate and the usual inorganic salts, *A. niger* gave no acetone, but formed glyoxylic, glycollic, and oxalic acids. The last acid was found by Raistrick and Clark (*loc. cit.*), the others have not previously been identified in this connexion. Dr. P. W. Clutterbuck has suggested to us that on analogy with oxidation processes in the animal organism, acetic acid is probably directly oxidised to glyoxylic acid, which, by dismutation, *i.e.*, the Cannizzaro reaction (Neuberg, *Ber.*, 1922, **55**, 3628), yields oxalic and glycollic acids.

The rapid disappearance of acetone from the citric acid cultures suggested a study of the action of the mould on this substance, but the suitable conditions for growth have not yet been ascertained.

The importance of saccharic acid in the sugar–citric acid fermentation has already been mentioned. Butkewitsch (*Biochem. Z.*, 1923, **142**, 205) was, however, unable to convert it into citric acid by *A. niger*, but this does not necessarily preclude its participation in the process. The conditions under which gluconic acid is converted into citric acid were only established after many failures (see p. 201) and it is possible that Butkewitsch was not working under the optimum conditions.

The authors find that when the mould has been grown on dipotassium saccharate for 4 to 5 weeks the culture gives a precipitate with mercuric sulphate and acidified potassium permanganate—Denigès's test—thus rendering the presence of citric acid probable. When the culture was distilled with potassium permanganate and dilute sulphuric acid, acetone was easily recognised in the distillate. Malic acid and ketonic acids give precipitates with mercuric sulphate and acidified potassium permanganate, but citric, acetoacetic, or acetonedicarboxylic acid would yield acetone on oxidation. The last two acids were shown to be absent. Aconitic acid gave no acetone on similar oxidation. Further work is necessary, however, before the production of citric acid from saccharic acid may be regarded as definitely established.

Experimental.

The medium employed throughout this research contained the following quantities (in grams) of hydrated salts per litre of water: ammonium nitrate, 0·356; potassium dihydrogen phosphate, 0·08; magnesium sulphate, 0·08; ferrous sulphate, 0·0046; zinc sulphate, 0·0046. This medium is hereafter designated solution M.

The fermentations were conducted in large flasks fitted with tubes for the withdrawal of samples under aseptic conditions. All

the mixtures were sterilised prior to inoculation, and great care was taken to prevent possible contamination by adventitious organisms. The cultures used for inoculation were all derived from Professor Neuberg's original strain, and when the work had been in progress for seven months, samples from one of the large reaction flasks were kindly examined by Miss M. Rhodes of the Lister Institute and certified as pure. All results were checked by control experiments performed simultaneously under identical conditions.

Fermentation of Citric Acid. Detection of Glyoxylic Acid.—Citric acid (50 g.) in 2500 c.c. of solution M was inoculated and incubated at 30°, and samples were tested frequently for glyoxylic acid. On the seventeenth day, a strong reddish-violet colour was obtained with naphtharesorcinol and hydrochloric acid, whereupon 2000 c.c. of the solution were withdrawn, filtered, and treated with 3 g. of aminoguanidine acetate in 100 c.c. of dilute acetic acid (1 : 1), giving after 48 hours a pale yellow solid (0·05 g.). On recrystallisation, this had m. p. 154° and melted at the same temperature in admixture with an authentic specimen of the aminoguanidine derivative of glyoxylic acid (Found by microanalysis: N, 37·4. Calc.: N, 37·9%). Döbner and Gärtner (*loc. cit.*) give the m. p. of this compound as 161°. Dakin (*J. Biol. Chem.*, 1906, **1**, 271) states that the compound does not melt very sharply, but after drying at 100° it has m. p. about 155°. The present authors find that the m. p. depends to some extent on the rate of heating.

Fermentation of Malonic Acid. Detection of Glyoxylic Acid.—Malonic acid (25 g.) in 2500 c.c. of solution M was inoculated and incubated at 30°. On the seventeenth day, a positive naphtharesorcinol test was obtained and 1000 c.c. of the filtered solution were then treated with 2 g. of aminoguanidine acetate and 50 c.c. of glacial acetic acid. After 48 hours, the deposit was separated (0·08 g.). It melted at 152·5°, and at 154·5° after recrystallisation from hot water. A mixture with a synthetic specimen (m. p. 155°) melted at 155° (Found: N, 37·5, 37·5%).

Fermentation of Citric Acid. Detection of Malonic Acid.—Citric acid (30 g.) in 2000 c.c. of solution M was inoculated and incubated at 30° and samples were tested daily with benzenediazonium chloride. On the eleventh day, a red precipitate was obtained, whereupon 600 c.c. of the fermenting liquid were filtered, cooled to 0°, and mixed with a well-cooled solution of benzenediazonium chloride (from 3 g. of aniline) in presence of excess of sodium acetate. After 24 hours, the red solid (2·9 g.) was washed with cold water, dried in a vacuum, and repeatedly crystallised alternately from aqueous methyl alcohol and benzene–light petroleum; it then

melted at 118—120°, alone or mixed with an authentic sample of hydrogen formazyl, m. p. 119°. It gave the characteristic dark green coloration with sulphuric acid (Bülow reaction) (Found : C, 69·7, 69·9; H, 5·5, 5·5; N, 25·2, 25·45. Calc. : C, 69·6; H, 5·4; N, 25·0%).

In another experiment, 2000 c.c. of the culture gave, on the tenth day, 1·3 g. of crude hydrogen formazyl.

Fermentation of Citric Acid. Isolation of Malonic Acid.—Citric acid (30 g.) in 2000 c.c. of solution M was inoculated and incubated as before. Malonic acid was detected on the tenth day, the whole of the solution (1900 c.c.) was filtered and concentrated under diminished pressure to 400 c.c., pure sodium carbonate added, and the slight excess neutralised with acetic acid. On evaporation, 43 g. remained, and 24 g. of this were well stirred with 60% alcohol in successive quantities of 25, 15, 15, and 10 c.c., and the extracts were evaporated. The residue (3·4 g.) was free from oxalate and citrate. When it was warmed with acetic anhydride and diluted with glacial acetic acid, the brown solution showed a strong greenish-red fluorescence—a reaction of malonic acid (Kleeman, *Ber.*, 1886, **19**, 2030). 1·5 G. were heated with 2 c.c. of glacial acetic acid and 30 drops of cinnamaldehyde in a sealed tube for 11 hours at 100°. Water (20 c.c.) and sodium carbonate were added, unchanged aldehyde was extracted with ether, and the alkaline solution was acidified, giving 0·6 g. of cinnamylidenemalonic acid. After recrystallisation, this melted at 207° and did not depress the m. p. (207°) of an authentic specimen. On exposure to light, it was superficially converted into a white solid (0·0214 and 0·0388 required 7·8 and 14·2 c.c. of *N*/40-NaOH. Calc., 7·85, 14·25). The alcoholic extract from the remainder (19 g.) of the evaporated culture was precipitated with aqueous lead acetate, and the lead salt decomposed by hydrogen sulphide. The white residue obtained on evaporation of the final filtrate gave, on extraction with ether, malonic acid (m. p. and mixed m. p. 132—133°, decomposing a few degrees above this temperature) (0·1002 and 0·1021 required 38·6 and 39·3 c.c. of *N*/20-NaOH. Calc., 38·55, 39·30).

Fermentation of Citric Acid. Detection of Acetone.—Citric acid (45 g.) in 2500 c.c. of solution M was fermented as usual and samples were tested daily for acetone by the iodoform reaction. This was given very faintly on the sixth day and strongly on the seventh day; 2200 c.c. of the solution were then filtered and neutralised with sodium hydroxide, and distilled. This distillate (800 c.c.) was mixed with 2000 c.c. of Denigès's reagent (50 g. of mercuric oxide in 1000 c.c. of water and 200 c.c. of sulphuric acid), and the whole heated under reflux at 100° for 40 minutes. The white precipitate was separated,

washed, dried (90 g.), and distilled, in portions of 15 g., with sodium iodide (30 g.) in 120 c.c. of water; 15 c.c. of distillate were collected in each case. A portion (55 c.c.) of the united distillates was mixed with acetone-free alcohol (60 c.c.), benzaldehyde (3 c.c.), and 10% sodium hydroxide solution (3 c.c.). The condensation product separated over-night and, after crystallisation from light petroleum, melted at 113° alone or in admixture with dibenzylideneacetone (Found: C, 86·6; H, 6·04. Calc.: C, 87·2; H, 6·0%).

The remainder of the distillate (35 c.c.) from the mercury compound was treated with *p*-nitrophenylhydrazine acetate; the product, after crystallisation from light petroleum, was identified as acetone-*p*-nitrophenylhydrazone by its m. p. (148·5°) and by the m. p., 149°, of a mixture with an authentic specimen.

Fermentation of Calcium Acetate. Detection of Glyoxylic Acid.—Calcium acetate (20 g.) in solution M (2000 c.c.) was inoculated and incubated at 32°. Glyoxylic acid made its appearance on the fifteenth day. 700 C.c. of the medium were then removed and filtered, made faintly acid to litmus with hydrochloric acid, neutralised with potassium hydroxide, and treated with 3·5 g. of aminoguanidine acetate in 50 c.c. of glacial acetic acid. After 5 days, 0·42 g. of crude condensation product was obtained. Two crystallisations from much hot water yielded 0·25 g. of m. p. 154° and mixed m. p. 154—155°.

Fermentation of Calcium Acetate. Isolation of Calcium Oxalate.—The remainder of the culture solution gradually deposited a white solid on the sides of the flask, and on the eighteenth day the mycelium was collected on a filter. The adhering solid was removed from the glass by warm 10% hydrochloric acid, which was then used for extracting the mycelium. The united extracts and washings (150 c.c.) were treated with a slight excess of ammonia, boiled for a few minutes, cooled, treated with a slight excess of 10% calcium chloride solution, and again boiled. The precipitate was well washed with much hot water and dried (Found: CaO, 43·9. Calc.: CaO, 43·75%).

Fermentation of Calcium Acetate. Isolation of Glycollic Acid.—Calcium acetate (60 g.) in 4000 c.c. of solution M showed, on the tenth day after inoculation, the presence of glycollic acid. Sulphuric acid, acetic acid, and 5% alcoholic *p*-cresol gave a dark green colour, whilst with sulphuric acid and alcoholic codeine (5%) a characteristic strong pink colour was obtained (Denigès, *Ann. Chim. phys.*, 1909, **18**, 178). The whole of the culture was filtered, treated with 60 g. of oxalic acid, this quantity being in large excess of that required to precipitate the calcium, and the deposit was separated and well washed. The filtrate, containing acetic acid,

excess of oxalic acid, and presumably glycollic acid, was treated with lead carbonate. The filtrate from the lead oxalate, containing the soluble lead salts, was treated with hydrogen sulphide, filtered, and evaporated to a syrup in a vacuum. This yielded 5·7 g. of white, transparent crystals, m. p. 68°, which were free from oxalic acid. After two crystallisations from dry ether–light petroleum, these melted at 79—80°, were indistinguishable in appearance from glycollic acid, and did not depress the m. p. (79—80°) of an authentic specimen (0·0508 required 13·40 c.c. of *N*/20-NaOH. Calc., 13·35 c.c. Found: C, 31·7; H, 5·2. Calc.: C, 31·6; H, 5·3%).

Fermentation of Potassium Saccharate. Detection of Citric Acid.—Potassium hydrogen saccharate (10 g.) was exactly neutralised by dilute aqueous potassium hydroxide, the usual inorganic salts were added in the proportions required by medium M, and the solution was diluted to 500 c.c., inoculated, and incubated at 31°. After being kept for 28 days at this temperature and for about a week at 20°, the solution gave a white precipitate with acidified mercuric sulphate solution and potassium permanganate, indicating the probable presence of citric acid.

200 C.c. of the culture were then acidified with sulphuric acid, slowly treated with aqueous potassium permanganate to oxidise any citric acid to acetonedicarboxylic acid, and slowly distilled. The distillate (50 c.c.), when heated with 200 c.c. of Denigès's mercuric sulphate solution (see p. 206), gave 3·8 g. of a white solid; this was distilled with 30 c.c. of water and 8 g. of sodium iodide. The distillate (5 c.c.), treated with 5 c.c. of alcohol, 5 drops of benzaldehyde, and 5 drops of 10% sodium hydroxide solution, gave dibenzylideneacetone, m. p. and mixed m. p. 113° (Found: C, 86·5; H, 6·1. Calc.: C, 87·2; H, 6·0%).

Potassium saccharate gave no acetone on similar oxidation. Distillation of the fermented medium gave no acetone, thus excluding the presence of acetoacetic and acetonedicarboxylic acids. Aconitic acid (5 g.) in 120 c.c. of dilute sulphuric acid (1 : 5) was oxidised with 200 c.c. of 3% potassium permanganate solution; the distillate (20 c.c.) gave only a minute trace of a precipitate when warmed under reflux with acidified mercuric sulphate.

The acetone obtained from the saccharate culture would therefore appear to have arisen from citric acid.

The expenses of this investigation have been in part defrayed by a grant from the Government Grant Committee of the Royal Society, for which the authors desire to express their thanks.

THE MUNICIPAL COLLEGE OF TECHNOLOGY AND THE UNIVERSITY, MANCHESTER. [*Received, November 20th,* 1926.]

XXXIII.—*Dicyanates and Dibenzoates of Triphenylbismuthine and Triphenylstibine.*

By Frederick Challenger and Vera Katharine Wilson.

From a consideration of the stability to heat of halogen and similar derivatives of the type Ph_3BiX_2, it was shown (J., 1926, 1648) that the halogens and pseudo-halogens could be arranged in an electrochemical order almost identical with that deduced by Birckenbach and Kellermann (*Ber.*, 1925, **58**, 786, 2377) from a study of the decomposition potentials of the potassium salts in aqueous solution.

Further evidence is now adduced as to the similarity of the conclusions reached by these entirely different modes of approach. Birckenbach and Kellermann showed that the electronegative properties of these elements and radicals decrease from fluorine thus: F, ONC, OCN, Cl, N_3, Br, CN, SCN, I, SeCN, TeCN. The position of the cyanate radical, OCN, is particularly interesting, since it is widely separated from the thiocyano- and selenocyano-groups. This difference has also been brought to light by a study of the properties of *triphenylbismuthine dicyanate*, $(C_6H_5)_3Bi(OCN)_2$. It is quite stable at the ordinary temperature, in marked distinction to the corresponding dithiocyanate and diselenocyanate, which lose phenyl pseudohalide. Its temperature of decomposition is about 150°, which is very close to that of triphenylbismuthine dichloride. The reaction is probably complex. Phenyl cyanate, Ph–O–CN, which should be produced according to the general equation $Ph_3BiX_2 = Ph_2BiX + PhX$ (J., 1922, **121**, 91), is unknown. If formed, it would doubtless undergo polymerisation and possibly other changes.

In comparing our results with those of Birckenbach and Kellermann, it has been assumed that triphenylbismuthine dicyanate has the normal cyanate structure, $Ph_3Bi(O{\cdot}C{:}N)_2$. Kaufmann and Kögler (*Ber.*, 1926, **59**, 184), from a comparison of the stabilities of the lead halides and pseudohalides, PbX_4, have reached identical conclusions as to the electrochemical order of F, OCN, and Cl, which give relatively stable derivatives. The thiocyanate, iodide and selenocyanate of this type decompose immediately according to the equation $PbX_4 = PbX_2 + X_2$.

The relative electrochemical positions of iodine and thiocyanogen were first investigated by Soderbäck (*Annalen*, 1919, **419**, 283). In aqueous or ethereal solution, an equilibrium exists between K(or Ag)SCN, K(or Ag)I, I_2, and $(SCN)_2$ and the results were inconclusive. Nitrosyl thiocyanate, however, has a transitory

existence in the deep red solutions obtained from nitrous acid and thiocyanates, or from nitrosyl chloride and silver thiocyanate. No evidence of the existence of the corresponding iodide can be obtained, but nitrosyl bromide is stable below −2°. On these grounds, he considered iodine to be the more positive radical. By a comparison of the times required for the development of the odour of iodobenzene and phenyl thiocyanate when triphenylbismuthine dichloride is mixed with aqueous solutions of potassium iodide and thiocyanate, results are obtained in agreement with those of Soderbäck and of Birckenbach and Kellermann (compare J., 1926, 1648). The observed times were 3 and 40 seconds, respectively, at the ordinary temperature, the theoretical quantities of the different salts being employed. The slower production of phenyl thiocyanate has been noted on several occasions and, indicating the slower decomposition of the dithiocyanate, is evidence of the more positive nature of iodine.

Wilkinson and one of us have shown (J., 1924, **125**, 856) that nitration of triphenylbismuthine dinitrate yields a meta-derivative. Owing to the oxidation of the triaryl derivatives (R_3M) of bismuth, antimony, arsenic, and phosphorus to compounds of the type $R_3M(O{\cdot}NO_2)_2$ during nitration, it was impossible to determine the orienting influence of the metal or metalloid in the tervalent condition.

From the work of Gelissen and Hermans (*Ber.*, 1925, **58**, 287) it appeared probable that, by the action of benzoyl peroxide on the triphenyl derivatives of the elements of the nitrogen group, mixed organo-derivatives such as $Ph_2Bi{\cdot}C_6H_4{\cdot}Ph$ or

$$PhCO{\cdot}O{\cdot}C_6H_4{\cdot}BiPh_2$$

might be obtained, according to the equations

(I.) $(PhCO)_2O_2 + Ph_2M{\cdot}C_6H_5 = PhCO_2H + CO_2 + Ph_2M{\cdot}C_6H_4{\cdot}Ph.$

(II.) $(PhCO)_2O_2 + Ph_2M{\cdot}C_6H_5 = PhCO{\cdot}O{\cdot}C_6H_4{\cdot}MPh_2 + CO_2 + PhH.$

The first reaction might be expected to predominate (Gelissen).

The dibromide or dichloride of a substance of the type $Ph_2M{\cdot}C_6H_4{\cdot}Ph$ might yield on suitable decomposition a halogen derivative of diphenyl, $C_6H_5{\cdot}C_6H_4X$ (J., 1915, **107**, 21, 23; 1924, **125**, 857): $(Ph{\cdot}C_6H_4)MPh_2X_2 = Ph{\cdot}C_6H_4X + Ph_2MX$. By orientation of the halogen atom in this compound, the directing influence of the tervalent element M might be determined. In boiling light petroleum, however, triphenylbismuthine and benzoyl peroxide gave *triphenylbismuthine dibenzoate*. The corresponding *stibine dibenzoate* was prepared in a similar manner. No other products could be isolated. The two dibenzoates were identical with the compounds obtained from silver benzoate and the bismuthine and

stibine dichlorides. Gelissen and Hermans (*Ber.*, 1926, **59**, 666) obtained a dibenzoate from *cyclo*hexene and the peroxide.

Triphenylphosphine and benzoyl peroxide in light petroleum at the ordinary temperature give triphenylphosphine oxide and benzoic anhydride, but no perbenzoic acid could be detected (compare Gelissen and Hermans, *Ber.*, 1926, **59**, 66). This illustrates the great tendency of the phosphorus atom in the phosphines to become quinquevalent, and is analogous to the action of thiocyanogen and thiocyanic acid giving the sulphide, Ph_3PS (J., 1923, **123**, 1054).

Difficulties in the preparation of triphenylphosphine (J., 1924, **125**, 864) may be avoided by using the method of Gilman and Vernon (*J. Amer. Chem. Soc.*, 1926, **48**, 1066), the crude undistilled triphenyl phosphite being treated directly with magnesium phenyl bromide. This method is much less troublesome than that involving the use of sodium and gives a much better yield.

Experimental.

Triphenylbismuthine dicyanate was prepared by shaking the dichloride (2·4 g.; 1 mol.) and silver cyanate (1·4 g.; 2 mols.) in dry ether (40 c.c.) for 4 hours. Extraction of the insoluble residue with chloroform yielded a solid which was crystallised twice from chloroform–light petroleum; m. p. 128·5—129°. A further quantity was obtained from the ether. The weight of silver chloride obtained was 1·30 g. (calc., 1·32 g.) (Found: C, 45·8, 45·8; H, 3·1, 3·2; N, 5·5, 5·4; Bi, 39·4, 39·1. $C_{20}H_{15}O_2N_2Bi$ requires C, 45·8; H, 2·9; N, 5·35; Bi, 39·9%).

When the dicyanate is warmed with aqueous alcohol (1:1), ammonia is evolved. On heating with excess of water, it gives a turbid, frothing liquid resembling an alkaline solution of the dichloride, and probably containing the unstable dihydroxide or oxide (J., 1920, **117**, 765). On heating to 150°, the dicyanate decomposes and an oil with an intensely pungent odour distils and partly solidifies. No definite product could be isolated from the minute amount available.

In one experiment, the silver cyanate used contained carbonate. The silver chloride precipitate then contained some insoluble triphenylbismuthine carbonate, which remained after removal of the dicyanate with chloroform and of silver salts with ammonia. With hydrochloric acid, it gave the dichloride, recognised by m. p. and mixed m. p.

Triphenylstibine Dicyanate.—Triphenylstibine dichloride (3·2 g.) and silver cyanate were shaken in dry ether for 14 hours. The solid was then washed with ether, leaving 2 g. of silver chloride (calc., 2·16 g.). The ether yielded 2·5 g. of white crystals, m. p. 105—113°. After two crystallisations from chloroform–light

petroleum, these melted at 111—112° (Found: N, 6·5, 6·4; Sb, 27·4, 28·1. $C_{20}H_{15}O_2N_2Sb$ requires N, 6·4; Sb, 27·9%).

Triphenylbismuthine and Benzoyl Peroxide.—An intimate mixture of these compounds reacted violently at 68°, white fumes and a strong odour of diphenyl being produced. Extraction with hot water and sodium hydroxide and crystallisation of the residue from alcohol yielded triphenylbismuthine and bismuth hydroxide. Other conditions were therefore employed.

The bismuthine (4 g.), benzoyl peroxide (2·2 g.; 1 mol.), and light petroleum (b. p. 60—80°; 50 c.c.) were heated under reflux. The clear solution soon deposited 3·3 g. of a faintly yellow solid, m. p. 164·5—166·5°. This was repeatedly crystallised from benzene–light petroleum, the last three operations giving products of m. p. 171·5–173·5°, 172—173·5°, 171—172·5°, taken simultaneously. The compound decomposed a few degrees above the m. p. With hot hydrochloric acid, it gave no benzene, indicating the absence of tervalent bismuth, but was converted into benzoic acid and triphenylbismuthine dichloride, m. p. 139—141°. When it was mixed with potassium iodide or thiocyanate in aqueous suspension, the characteristic odours of iodobenzene and phenyl thiocyanate were produced, thus affording conclusive proof of the presence of a derivative of quinquevalent bismuth (J., 1922, **121**, 92; 1924, **125**, 854). Analysis showed the substance to be *triphenylbismuthine dibenzoate*, and it did not depress the m. p. of the product obtained from the dichloride and silver benzoate (Found: Bi, 30·8, 30·5. $C_{32}H_{25}O_4Bi$ requires Bi, 30·6%).

The petroleum mother-liquor from the original reaction was concentrated, yielding successively benzoyl peroxide, triphenylbismuthine dibenzoate, and triphenylbismuthine.

Triphenylstibine and Benzoyl Peroxide.—From the stibine (5 g.) and the peroxide (3·4 g.; 1 mol.) in light petroleum (b. p. 60—80°; 100 c.c.), a solid, m. p. 170·5—173·5°, separated after 20 minutes' heating (7·3 g.). After two crystallisations from benzene–light petroleum, it melted at 171·5°, the purification being less troublesome than that of the corresponding bismuth compound. With hot hydrochloric acid, the stibine dichloride (m. p. and mixed m. p. 142—143°) and benzoic acid, m. p. 121°, were obtained. The original petroleum filtrate yielded a trace of triphenylstibine.

Analysis showed the product to be *triphenylstibine dibenzoate*. It did not depress the m. p. (170·5—172·5°) of the compound obtained from the dichloride and silver benzoate (Found: Sb, 20·4, 20·6. $C_{32}H_{25}O_4Sb$ requires Sb, 20·5%).

A comparison of the m. p.'s of the dichlorides and dibenzoates of triphenylbismuthine and triphenylstibine is of interest:

	Dibenzoate.	Dichloride.
Bismuthine	172—173°	141°
Stibine	171—171·5	143

Preparation of the Bismuthine and Stibine Dibenzoates from the Corresponding Dichlorides.—(*a*) Bismuthine dichloride, 2 g.; (*b*) stibine dichloride, 0·9 g. Silver benzoate (2 mols.) (*a*) 1·8 g., (*b*) 0·95 g. Reaction occurred on shaking in chloroform over-night. The product, purified as described above, had m. p. (*a*) 171·5°, (*b*) 170·5—172·5°.

Triphenylphosphine and Benzoyl Peroxide.—The phosphine (2·9 g.) and the peroxide (2·7 g.; 1 mol.) were separately and completely dissolved in light petroleum, and the cold solutions mixed. A precipitate quickly formed which melted at 140—148°, and after three crystallisations from chloroform–light petroleum had the constant m. p. 153·5°. It did not depress the m. p. (153·5°) of an authentic specimen of triphenylphosphine oxide.

The original petroleum filtrate on concentration deposited white crystals, m. p. 37·5—39·5°. These were free from phosphorus (and from perbenzoic acid, as shown by the odour and by the behaviour to both aniline and potassium iodide) and when mixed with benzoic anhydride (m. p. 42·5—43·5°) also melted at 37·5—39·5°. The compounds appeared to be identical. With warm aniline, the product from the reaction quickly gave benzanilide, m. p. and mixed m. p. 159—160°, but no nitrosobenzene.

When the phosphine and the peroxide were shaken in the minimum of light petroleum for an hour, heat was developed. The products of the reaction were the same.

The authors wish to express their thanks to the Research Fund Committee of the Chemical Society for a grant which has defrayed the expenses of this investigation.

THE UNIVERSITY, MANCHESTER. [*Received, November 13th*, 1926.]

XXXIV.—*Acid and Salt Effects in Catalysed Reactions. Part IV. Derivation of a General Equation for the Catalytic Activity of Acids. The General Catalytic Catenary.*

By HARRY MEDFORTH DAWSON.

THE results of experiments described in previous papers (Dawson and Carter, J., 1926, 2282; Dawson and Dean, *ibid.*, p. 2872; Dawson and Hoskins, *ibid.*, p. 3166) show that the catalysing power

of acid–salt mixtures of the type cHA + xMA (c constant and x variable) is such that, in general, the reaction velocity falls as x increases, reaches a minimum, and then increases continuously according to the linear formula $v = a + bx$. The curves which are obtained by plotting the reaction velocity against the p_H value of the catalysing solution are symmetrical with respect to the point at which the velocity is a minimum.

In accordance with the equations for the hydrogen-ion concentration $[H^+]_i$ and the velocity v_i which characterise the minimum velocity (*M.V.*) mixture, namely,

$$[H^+]_i = \sqrt{k_a Kc/(k_h - k_m)}$$

and

$$v_i = 2\sqrt{(k_h - k_m)k_a Kc} + k_m c$$

it has also been shown that for a given acid $[H^+]_i$ is directly proportional to the square root of the acid concentration, and that the specific minimum velocity v_i/c is a linear function of the square root of the dilution of the acid.

It follows that the reaction velocities for all possible mixtures of an acid with its corresponding salts can be represented on the v–p_H diagram by a sheaf of curves which are catenary in type. The dimensions of the individual catenaries and the positions of their apices (the *M.V.* points) are determined by the nature of the acid and its concentration. The influence of the nature of the acid finds expression in the catalytic coefficients, k_h, k_a, and k_m for the hydrogen ion, the acid anion, and the undissociated acid molecule, respectively, and in the ionisation constant, K, of the acid. The catenary curves on the v–p_H diagram, it may be noted, should really be considered as the projections on this plane of catenary surfaces, the complete representation of which would necessitate the use of a tridimensional co-ordinate system with reaction velocity, acid concentration, and p_H as the respective co-ordinates.

Although the observations already described are such as to suggest that the relations involved are of general character, it may now be pointed out that similar catalytic phenomena have been met with as a result of the preliminary examination of many other acids. Amongst these may be mentioned oxalic acid (both in the first and second stages of dissociation), tartaric acid (first and second stages), phosphoric acid (first and second stages), and sulphuric acid (second stage). In the case of the strongest acids (such as the halogen acids, nitric acid, etc.), there is, however, no initial fall, but, on the other hand, the velocity increases continuously with the concentration of the added salt. It will be shown in due course that this behaviour of the strongest acids is

not inconsistent with the views which have been developed on the basis of observations made with weaker acids.

In the circumstances, it seems desirable at this stage to indicate that the theory outlined in the previous papers of this series leads to a general formula for the catalytic effects produced by acids which, in view of its simplicity, would seem to be of considerable importance. This general formula follows directly from the equation

$$v = v_h + v_a + v_m = k_h[H^+] + k_a[A^-] + k_m[HA] \quad . \quad . \quad (1)$$

the only assumption involved being that the dissociation of the acid conforms to the requirements of the mass law. Substituting for $[A^-]$ the value given by $[A^-] = K(c - [H^+])/[H^+]$ and for $[HA]$ the value $c - [H^+]$, and rearranging the terms, we get

$$v = (k_h - k_m)[H^+] + k_aKc/[H^+] + k_mc - k_aK \quad . \quad . \quad (2)$$

For a fixed acid concentration, the variations in velocity are due to changes corresponding with the first two terms, and if the ionic reaction velocity is denoted by u, we may write

$$u = v_h + v_a = (k_h - k_m)[H^+] + k_aKc/[H^+] \quad . \quad . \quad (3)$$

If the hydrogen-ion concentration $[H^+]$ is expressed in terms of the hydrogen-ion concentration $[H^+]_i$ of the corresponding *M.V.* mixture, such that $[H^+] = n[H^+]_i$, then equation (3) may be written

$$u = (k_h - k_m)n[H^+]_i + k_aKc/n[H^+]_i,$$

and since $[H^+]_i = \sqrt{k_aKc/(k_h - k_m)}$,

we have $$u = \sqrt{(k_h - k_m)k_aKc}(n + 1/n) \quad . \quad . \quad . \quad . \quad (4)$$

Since, further, the minimum ionic velocity u_i is given by

$$u_i = 2\sqrt{(k_h - k_m)k_aKc} \quad . \quad . \quad . \quad . \quad (5)$$

we obtain by combination of (4) and (5)

$$r = u/u_i = \tfrac{1}{2}(n + 1/n) \quad . \quad . \quad . \quad . \quad . \quad (6)$$

In equation (6), n represents the hydrogen-ion concentration of any solution in terms of that of the corresponding *M.V.* mixture, and may be termed the reduced hydrogen-ion concentration. Similarly, r expresses the velocity due to the hydrogen and acid anions for any solution in terms of the ionic reaction velocity of the corresponding *M.V.* mixture and may be called the reduced ionic reaction velocity.

If $\log_{10} n = (p_H)_i - p_H$ be denoted by Δp_H, then Δp_H may be referred to as the reduced p_H value of the solution in question, and equation (6) may be written in the form

$$r = \tfrac{1}{2}(10^{\Delta p_H} + 10^{-\Delta p_H}) \quad . \quad . \quad . \quad . \quad . \quad (7)$$

This is the equation of a catenary, and it expresses quite generally the connexion between the reduced ionic velocity and the reduced p_H value for any catalysing solution. Its applicability would appear to be independent of the nature and concentration of the catalysing acid, of the temperature, of the nature of the solvent, and also of the nature of the catalysed reaction. It is therefore to be regarded as a general formula applicable to all catalysed reactions in so far as the velocity of these depends on the positive hydrogen ions and the corresponding negative anions.

It follows that the ionic reaction velocities for any acid-catalysed reaction should be representable by a single catenary curve. Equation (7) and the corresponding curve obtained by plotting the reduced ionic reaction velocity against the reduced p_H value may be termed the reduced or general catalytic catenary.

It may be noted that, in the derivation of this relation, the procedure followed is analogous to that by which the specific gas equations of the ordinary type are transformed into general reduced equations of condition.

The mathematical form of the general equation may be further simplified, for if the natural logarithm of the reduced hydrogen-ion concentration is denoted by h, *i.e.*, if $\log_e n = h$, then this equation may be written

$$r = \cosh h \quad . \quad . \quad . \quad . \quad . \quad . \quad (7a)$$

according to which, the reduced ionic velocity is equal to the hyperbolic cosine of the logarithm of the reduced hydrogen-ion concentration. There are obvious reasons, however, for regarding equation (7) as the more convenient form of the general relation.

Significance of the Reduced Catalytic Catenary.

The experimental data on which the foregoing views are based have reference to the catalytic behaviour of acid–salt mixtures represented by $c\mathrm{HA} + x\mathrm{MA}$, in which c is constant and x is variable. In accordance with the view that the salt is completely ionised, this series of mixtures may be represented by $c\mathrm{HA} + x\mathrm{A}^-$, for the positive ion M^+ has no measurable catalytic activity.

The symmetry of the reduced catalytic catenary obviously suggests the possibility of a complementary series corresponding with the formula $c\mathrm{HA} + x'\mathrm{H}^+$, but it does not follow that the latter can be actually realised, for although it is very probable that the strongest acids are very largely ionised, there is evidence to support the view that the ionisation is not complete. Since the non-ionised acid would appear to be a very active catalyst, it is clear that there may be a considerable difference in practice between the two stoicheiometrically complementary series of solutions.

If, however, it is assumed that the ionisation of a strong acid, *e.g.*, hydrochloric acid, is practically complete in dilute solution, and that the catalytic activity of the chlorine ion is negligible in comparison with that of the hydrogen ion, it should be possible to realise to a limited extent the series of solutions which is represented by $c\mathrm{HA} + x'\mathrm{H}^+$.

The dividing line between the stoicheiometrically complementary series of catalysing solutions corresponds with $x = x' = 0$. This corresponds with a solution of the free acid HA and it may be shown that this is represented by a point on the reduced catalytic catenary, the position of which is determined solely by the relative magnitudes of the catalytic coefficients k_h, k_a, and k_m.

It will be assumed that the acid concerned is weak and that the hydrogen-ion concentration $[\mathrm{H}^+]_0$ of the pure acid solution is given with sufficient exactness by the mass-law expression $[\mathrm{H}^+]_0 = \sqrt{Kc}$. We may then write

$$u_0 = (k_h - k_m)\sqrt{Kc} + k_a\sqrt{Kc},$$

and since

$$u_i = 2\sqrt{(k_h - k_m)k_aKc},$$

we obtain by division

$$r_0 = u_0/u_i = \tfrac{1}{2}\left(\sqrt{(k_h - k_m)/k_a} + \sqrt{k_a/(k_h - k_m)}\right) \quad . \quad . \quad (8)$$

where r_0 denotes the reduced ionic velocity for the pure acid solution.

From equations (6) and (8) it is apparent that the reduced ionic concentration of solutions of the pure acid is given by $n_0 = \sqrt{(k_h - k_m)/k_a}$, whence

$$(\Delta p_{\mathrm{H}})_0 = \log_{10}\sqrt{(k_h - k_m)/k_a} \quad . \quad . \quad . \quad . \quad (9)$$

It is thus evident that the position of the point H_0 on the catenary is determined by the magnitude of the catalytic coefficients for the acid in question.

Since the relative magnitudes of the catalytic coefficients vary widely according to the strength of the acid and according to the nature of the catalysed reaction, it is obvious that the experimental realisation of the catenary curve may be achieved much more readily with some reactions than it is with others. For such reactions as ester hydrolysis and sucrose inversion, it would seem that the coefficients k_a and k_m are very small in comparison with k_h.

According to the evidence which is available for the acetone–iodine reaction, k_m can be neglected in comparison with k_h in the case of weaker acids, whilst the ratio k_h/k_a increases with increasing strength of the acid as measured by the dissociation constant K.

Catalytic Effects due to the Hydrogen and Hydroxyl Ions.

In accordance with the very general character of the reduced catalytic catenary, it is not surprising that the catalytic effects produced by the simultaneous action of the hydrogen and hydroxyl ions should conform to the requirements of equation (7). This, indeed, may be regarded as a particular case of catalytic action in which the hydrogen ion and the acid ion (hydroxyl) are derived from or are controlled by the solvent.

The equation for the velocity of reaction may be written

$$v = k_h[H^+] + k_{OH}[OH^-] + k_m[H_2O],$$

and since $[H^+].[OH^-] = K_w$ and $[H_2O]$ is constant, it follows that the ionic velocity u is given by

$$u = k_h[H^+] + k_{OH} \cdot K_w/[H^+].$$

The reaction velocity is a minimum when the hydrogen-ion concentration has the value $[H^+]_i = \sqrt{k_{OH} \cdot K_w/k_h}$. Substituting this in the equation for u we obtain

$$u_i = 2\sqrt{k_h \cdot k_{OH} \cdot K_w},$$

whence

$$\begin{aligned} r &= \tfrac{1}{2}([H^+]/[H^+]_i + [H^+]_i/[H^+]) \\ &= \tfrac{1}{2}(n + 1/n) \\ &= \tfrac{1}{2}(10^{\Delta p_H} + 10^{-\Delta p_H}), \end{aligned}$$

or the same result as that which was obtained for the reduced ionic velocity due to the joint catalytic effect of any acid HA in conjunction with the corresponding salt.

In view of the very weak acidic character of water, it is probable that the magnitude of the coefficient k_m is very small in comparison with k_h and k_{OH}, in which case the ionic velocity u is identical with the actually measured velocity v.

The main difference between the catalytic effects which are produced by the combined action of the hydrogen and hydroxyl ions, as compared with those which have been observed for the catalysing action of acid–salt mixtures in the acetone–iodine reaction, lies in the fact that k_{OH}/k_h is greater than unity, whilst for the acids used in the acetone experiments k_a/k_h is less than unity.

A reaction in which the joint action of hydrogen and hydroxyl ions has been studied is the hydrolysis of methyl acetate at 25°, for which, according to Wijs (*Z. physikal. Chem.*, 1893, **11**, 492; **12**, 514), the value of k_{OH}/k_h is about 1400, and since the hydrogen-ion concentration corresponding with minimum reaction velocity is given by $[H^+]_i = \sqrt{k_{OH}K_w/k_h}$, it follows that $(p_H)_i = 5{\cdot}43$ if K_w is equal to 10^{-14}. The neutral point characterised by $p_H = 7$ lies,

therefore, on the right-hand side of the catalytic catenary. In these circumstances, it is obvious that the addition of acid ion (hydroxyl) in the form of, say, sodium hydroxide to pure water will not diminish, but on the contrary, will increase the reaction velocity, and that the attainment of the *M.V.* point will necessitate the diminution of the hydroxyl-ion concentration by the addition of hydrogen ions. The so-called neutral point for water corresponds in the more general case with a solution of the free acid HA, the hydrogen-ion concentration of which has already been denoted by $[H^+]_0$. The H_0 points are characterised by equality of the concentrations of the hydrogen ion and the corresponding anion, whereas the H_i points are distinguished by the equality of the catalytic effects which are produced by the positive and negative ions. Since $(\Delta p_H)_0 = \frac{1}{2} \log (k_h - k_m)/k_a$, it is clear that the H_0 point will be situated on one branch of the catalytic catenary if the ratio $(k_h - k_m)/k_a$ is greater than unity, and on the other branch if the ratio is less than unity. When k_m can be neglected in comparison with k_h, the relative positions of the H_0 and H_i points will be determined by k_h/k_a.

The relations described point strongly to the undesirability of differentiating between the hydroxyl ion and other acid ions. The catalytic behaviour of the hydroxyl ion is indeed so closely similar to that of other acid ions that there appears to be no valid reason for the commonly accepted view that the hydroxyl ion is distinguished from other negative ions in its catalytic properties. In due course, experiments will be described which show directly that negative ions, other than hydroxyl, have very highly developed catalytic activity.

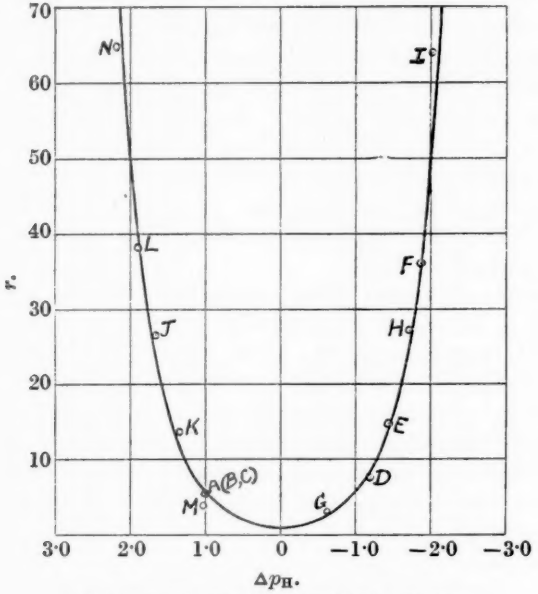
Testing the Reduced Catalytic Catenary.

The data available for submitting the general catalytic catenary to the test of experiment are limited to those furnished by observations on the velocity of the acetone–iodine reaction and to Karlsson's data (*Z. anorg. Chem.*, **1921**, **119**, 69) for the rate of hydrolysis of methyl and ethyl acetates at 85·5° in aqueous solutions buffered by the addition of mixtures of acetic acid and sodium acetate. The p_H values of these buffered solutions were determined electrometrically at 85·5° and from a series of observations with each of the two esters Karlsson has derived the minimum reaction velocities and the corresponding $(p_H)_i$ values, a knowledge of which is required for the purpose of the test.

Critical inspection of Karlsson's data shows that the accuracy attained in the individual experiments is not of a high order, and for this reason it is only possible to consider those observations in

which the effect of errors of experiment is as small as possible. Whatever the nature of the catalysed reaction, the nearer we approach the apex of the catalytic catenary, the more accurate must be the measurements if they are to be utilised for the purpose of testing the general equation which has been derived.

The accompanying diagram shows the general catalytic catenary with r as ordinate and Δp_{H} as abscissa. The points shown on the diagram and indicated by capital letters refer to experimental observations, the nature of which is summarised in the table on



The general or reduced catalytic catenary.

p. 221. Subject to the above consideration, the observations have been selected from the available material so as to cover as wide a range as possible. In the case of the acetone–iodine reaction—points A to K—the observations include data for both acetic and chloroacetic acids in the presence and absence of the corresponding salts. The table gives the values of p_{H}, $(p_{\mathrm{H}})_i$, v, v_i, u, and u_i, from which the required values of Δp_{H} and r have been computed. The numbers expressing the reaction velocities are the actual velocities in g.-mols. per litre per minute multiplied by 10^6. Karlsson's numbers have therefore been multiplied by 2·30.

In reference to the table of results it should be noted that the data for the 0·05, 0·1, and 0·2N-acetic acid solutions (points A, B, and C) give values for r and Δp_{H} which are identical within the limits of

TABLE I.

Characterisation of the Points included in the Diagram of the General Catalytic Catenary.

Nature of catalyst or catalysed reaction.	p_H.	$(p_H)_i$.	Δp_H.	v.	v_i.	u.	u_i.	r.
A. 0·05*N*-$CH_3{\cdot}CO_2H$.	3·01	4·03	+1·02	0·50	0·164	0·425	0·089	4·8
B. 0·1*N*-$CH_3{\cdot}CO_2H$.	2·87	3·88	+1·01	0·75	0·273	0·60	0·123	4·9
C. 0·2*N*-$CH_3{\cdot}CO_2H$.	2·72	3·72	+1·00	1·16	0·465	0·86	0·165	5·2
D. 0·05*N*-$CH_3{\cdot}CO_2H$ + 0·16*N*-$CH_3{\cdot}CO_2Na$.	5·24	4·03	−1·21	0·724	0·164	0·649	0·089	7·3
E. 0·1*N*-$CH_3{\cdot}CO_2H$ + 0·4*N*-$CH_3{\cdot}CO_2Na$.	5·33	3·88	−1·45	1·95	0·273	1·80	0·123	14·6
F. 0·1*N*-$CH_3{\cdot}CO_2H$ + 1*N*-$CH_3{\cdot}CO_2Na$.	5·73	3·88	−1·85	4·60	0·273	4·45	0·123	36·2
G. 0·2*N*-$CH_3{\cdot}CO_2H$ + 0·1*N*-$CH_3{\cdot}CO_2Na$.	4·33	3·72	−0·61	0·775	0·465	0·475	0·165	2·9
H. 0·2*N*-$CH_3{\cdot}CO_2H$ + 1*N*-$CH_3{\cdot}CO_2Na$.	5·43	3·72	−1·71	4·80	0·465	4·50	0·165	27·2
I. 0·2*N*-$CH_3{\cdot}CO_2H$ + 2*N*-$CH_3{\cdot}CO_2Na$.	5·73	3·72	−2·01	10·9	0·465	10·6	0·165	64
J. 0·1*N*-$CH_2Cl{\cdot}CO_2H$.	1·91	3·56	+1·65	7·75	2·60	5·35	0·20	26·7
K. 0·1*N*-$CH_2Cl{\cdot}CO_2H$ + 0·02*N*-$CH_2Cl{\cdot}CO_2Na$.	1·21	3·56	+1·35	5·12	2·60	2·72	0·20	13·6
L. Hydrolysis of methyl acetate.	2·83	4·70	+1·87	1220	32	1220	32	38
M. Hydrolysis of methyl acetate.	3·69	4·70	+1·01	122	32	122	32	3·8
N. Hydrolysis of ethyl acetate.*	2·85	5·05	+2·20	980	15	980	15	65

* The values assigned by Karlsson to $(p_H)_i$ and u_i for the hydrolysis of ethyl acetate are 5·10 and $6{\cdot}8 \times 10^{-6}$, respectively. The values adopted in the table are 5·05 and $6{\cdot}5 \times 10^{-6}$, which would appear to be more nearly in accordance with the graph of Karlsson's experimental data.

error. This result is entirely in accordance with equations (8) and (9), which give respectively $r = 5{\cdot}0$ and $\Delta p_H = 0{\cdot}99$, values which are independent of the concentration of the acid.

Having regard to the nature of the variations which are represented in the table and on the diagram—variations in the nature of the catalysed reaction, in the nature and type of the catalyst, and in the temperature of the respective observations—the concordance between the experimental data and the theoretical deductions is such as to justify the belief that the reduced catalytic catenary represents a very general expression for the effects produced by the joint action of the catalytically active ions which are formed by the dissociation of acids.

Finally, it may be noted that the movement of an index point along the general catenary from left to right represents, not only the changes in catalytic activity which are produced by the addition of a salt to the corresponding acid, but also a continuous series of H_0 points corresponding with pure acids for which the relative

catalytic activity of the acid anion increases whilst the ionisation constant decreases.

Summary.

A general equation for the velocity of chemical change has been derived which expresses the catalytic effects produced by acids, either alone or in the presence of the corresponding salts.

This equation may be written in the form

$$r = \tfrac{1}{2}(10^{\Delta p_H} + 10^{-\Delta p_H}),$$

in which r is the velocity due to the positive and negative ions expressed in terms of the velocity for the corresponding *M.V.* mixture, and Δp_H is the difference between the p_H values of the solution in question and of the *M.V.* mixture.

The above expression, which corresponds with a catenary curve, may be termed the general or reduced catalytic catenary. It appears to be capable of very wide application and is independent of the nature of the catalysing acid, of its concentration, of the temperature, of the nature of the solvent, and of the type of the catalysed reaction.

The general catalytic catenary has been tested by reference to the data which are available for the purpose.

UNIVERSITY OF LEEDS. [*Received, November 24th*, 1926.]

XXXV.—*The Liesegang Phenomenon and Stratification.**

By MAURICE COPISAROW.

THE present study of colloidal and stratified calcium carbonate, not only completes the investigation on the heteromorphism of this substance (J., 1923, **123**, 785), but also shows that neither organised life nor organic hydroxy-compounds, and—more remarkable still—neither colloid, at least of a permanent character, nor suspended matter, is essential in the formation of strata. Nevertheless, although only hydration is necessary for the stratification of calcium carbonate, yet, as is shown later, the presence of colloids and salts and experimental conditions, such as temperature and pressure, which influence hydration, greatly affect the nature of the product. Thus, whilst hydrocalcite ($CaCO_3,5H_2O$) (Copisarow, *loc. cit.*) represents the maximum state of hydration under normal conditions, a hexahydrate is obtained in sugar solution, etc. (Pelouze, *Compt. rend.*,

* Publication of this work, which was carried out during 1923—24, long before the appearance of Ganguly's paper (J., 1926, 1381), has been delayed owing to the illness of the author.

1865, **60**, 429; Mackenzie, J., 1923, **123**, 2409). Again, whilst ordinarily the dehydration of calcium carbonate * is complete at 18—20°, yet in the case of mother-of-pearl (formed in presence of "conchiolin") apparently a dihydrate persists up to 50°, at which temperature the mother-of-pearl loses its iridescence, becoming "dead." †

Cohesion, hitherto elusive, not only in synthetically prepared calcium carbonate of the stratified variety, but also in all cases of Liesegang ring formation, is certainly dependent upon velocity of formation and pressure. The influence of pressure upon cohesion is well illustrated by the synthesis of marble and alabaster (Copisarow, *loc. cit.*). Unfortunately, owing to lack of facilities, the study of pressure and the time factor upon Liesegang rings in general, and rings of calcium carbonate in particular, could not be carried out.

Considering the peculiarities of the stratification of calcium carbonate itself, we find that it is the first case in which (*a*) Liesegang rings, (*b*) opacity bands, and (*c*) tree formation make a joint appearance. This combination of occurrences may be regarded as an extension of the Liesegang phenomenon, rather than an anomaly of it.

The fibrillar structure of the colloidal calcium carbonate formed *in situ* supplies the necessary framework for the ring formation, and at the same time accounts for its peculiar physical properties. The presence of colloidal calcium carbonate and the general mild conditions explain the formation of opacity regions, which, being the outcome of the mild effect of an electrolyte upon a colloid, may be regarded as very diffused Liesegang rings. This formation of opacity bands of colloidal calcium carbonate (the concentrations of which progress in opposite directions to one another) is identical with the observations of Holker (*Proc. Roy. Soc.*, 1923, *A*, **102**, 710), the distinguishing feature between the two being that Holker's whole series of test-tube experiments is naturally embodied in one phenomenon, taking place in one vessel. The tree formation, as an extreme case of spiral deformation of Liesegang rings, may be regarded as being due, on the one hand, to strong diffusion and, on the other, to the transformation of a semipermeable membrane to an impermeable one owing to the dehydration of calcium car-

* Hydrocalcite, $CaCO_3,5H_2O$ (Pfeiffer, *Arch. Pharm.*, 1879, **15**, 212; Copisarow, *loc. cit.*), and subhydrocalcite, $CaCO_3,3H_2O$ (Ivanow, *Z. Kryst. Min.*, 1908, **44**, 87; Copisarow, *loc. cit.*), are the only mineral hydrated forms of calcium carbonate. $CaCO_3,2H_2O$ (mother-of-pearl?) and $CaCO_3,6H_2O$ are formed in presence of organic matter only.

† Clément and Rivière (*Compt. rend.*, 1922, **174**, 1353) gave the following analysis of mother-of-pearl:

$CaCO_3$, 75; H_2O, 25; albumin, 5% ($CaCO_3,2H_2O$ requires H_2O, 26·7%).

bonate. In this case, diffusion takes place at one or more points of least resistance instead of throughout the whole membrane.

Extremes in reactivity and in conditions of experiment are detrimental to the periodic effect. The electrolyte, to be effective, must be strong enough to cause orientation, coagulation, or " salting out " in the medium (electrolyte, colloid, or matter in suspension). Opacity bands, produced by salt solutions acting upon colloids (Holker, *loc. cit.*), by ammonia gas upon gelatin (see later), and by the interaction of calcium chloride with sodium carbonate, indicate the phenomenon of periodicity, but are not strong enough to condense these wide bands to a series of rings or membranes.

The Liesegang phenomenon is complex in character, and the actual rings are the outcome of a primary and a secondary cause. The primary cause is the periodic deformation or coagulation of the fibrillar structure of the colloid, under the influence of the electrolyte. The secondary cause, contributing to the viscosity and thickness rather than to the formation of the rings, is the salting out or deposition of the electrolyte on the coagulated membrane. Thus the usual Liesegang rings represent an intimate mixture of electrolyte and colloid. The fact that the secondary cause may be eliminated without interfering with the first or periodic effect, is shown by the action of hydrochloric acid, ammonia, or formaldehyde on gelatin, described later. Not infrequently, cases are encountered where the initial substances taking part in the Liesegang formation are neutral in character, but in these cases we often find hydrolysis or reduction preceding ring formation, acidic or basic bodies being produced *in situ*.

The general study of the Liesegang phenomenon in this paper revealed the possibility of substituting in ring formation the two salt and the one salt–acid systems (Moeller, *Kolloid Z.*, 1917, **20**, 242) by (1) one basic salt (sodium carbonate, baryta, etc.), and (2) a gas or its aqueous solution (hydrogen chloride, formaldehyde, ammonia, etc.).

These facts, together with the observation that Liesegang rings may be formed in an aqueous medium (*e.g.*, solutions of calcium chloride and sodium carbonate), widen considerably the whole aspect of the Liesegang phenomenon and show definitely the inadequacy of any single theory, hitherto advanced, to afford a proper explanation.

The influence of light, studied by several investigators (Davies, *J. Amer. Chem. Soc.*, 1923, **45**, 2261; Tryhorn and Blacktin, *Trans. Faraday Soc.*, 1923, **19**, 433), is to a large extent accounted for by the photochemical changes it induces, but it also involves a milder and much more general effect, that of local activation, or

formation of nuclei. Careful study of the tree formation showed that in more than 70% of the cases the direction of the spiral tended towards the illuminated side of the vessel no matter where the trees originated. After fully considering such disturbing factors as the sensitiveness of the trees to traffic-vibration, reflexion, and general difficulty of localising the light, the influence of light upon orientation can scarcely be doubted. This finds ready support in the fact that when sodium carbonate solution acted upon a set gelatin solution of calcium carbonate, the reaction taking place in a glass cylinder of 2·5 cm. diameter, the Liesegang rings were not horizontal, though parallel to one another. The rings seemed to incline invariably towards the illuminated side of the vessel, suggesting that diffusion, and therefore interaction, was more rapid on that side.*

Experimental.

Section I. (With George Ernest Wilson.)

Ring Formation with One Basic Salt.

Sodium Carbonate.—Series 1; 1% *solution.* Graduated test tubes (2 cm. × 15 cm.) containing a set solution of gelatin † (5—8 cm. in height) were almost filled with a 1% sodium carbonate solution and allowed to stand. At the salt–gelatin junction, a translucent concave membrane soon formed. On further standing, rings gradually appeared below this membrane, and examination showed them to be considerably thicker than the membrane. Under the magnifying glass, they were seen to consist of a multitude of fine globules, in the form of a gelatinous precipitate, the compactness of packing diminishing upwards. The inter-band distances progressively increased with each succeeding ring. After 7 days, 4 bands appeared, increasing to 6 at the end of 14 days. Measurements by means of a cathetometer gave the following figures: After 7 days, the membrane had moved down 0·2 cm., the curvature of meniscus was 0·1 cm., and the distances from the position of the membrane to the consecutive bands ‡ were 0·4, 0·8, 1·3, and 1·9 cm.,

* Some years ago, the author made similar observations on the crystallisation of certain substances from solution. Mere evaporation would scarcely account for the invariable primary appearance of the crystals on the more illuminated side of the vessel. Davies (*loc. cit.*) found that light influenced ring formation in a medium of colloidal gold.

† In all the experiments "Gelatine extra" of Coignet Père, Fils, et Cie. was used, the solutions (usually 5%) being employed within 12 hours of their preparation. The experiments were carried out in a basement having a concrete floor, so as to eliminate as far as possible the effect of light and vibration.

‡ In all measurements, the edge of the membrane was taken as an indication of its position, as, owing to diffusion and osmotic pressure, the mem-

respectively. After 14 days, the membrane had moved down 0·5 cm., the curvature was 0·25 cm., and the distances from the *new* position of the membrane to the consecutive bands were 0·7, 0·9, 1·4, 2·1, 2·8, and 3·5 cm., respectively.

The number of bands formed after 7 and 14 days, given above, does not really indicate the rate of formation of bands, as the membrane in its movement downwards first depresses the bands and then absorbs them. But even after 3 months, when the diffusion was complete, the adhesion of the remains of the bands to the walls of the tube was sufficiently strong to leave a record of their original position.

Series 2; 5% *solution.* When experiments were carried out as in series 1, but with a 5% solution of sodium carbonate, the texture of the bands was more compact, and the inter-band spaces were comparatively smaller.

After 2 days, 7 bands had formed; membrane (concave) had moved down 0·5 cm. from original position; curvature of meniscus, 0·1 cm.; distances from membrane to consecutive bands were 0·6, 0·9, 1·2, 1·5, 2·0, 2·5, 3·1 cm., respectively.

After 7 days, 9 bands had formed; membrane had moved down 0·9 cm. from original position; curvature of meniscus, 0·4 cm.; distances of bands from new position of membrane, 1·0, 1·2, 1·5, 1·9, 2·4, 3·0, 3·7, 4·5, 5·4 cm., respectively, the bands reaching the bottom of the tube.

After 14 days, 8 bands remained; membrane had moved down 1·5 cm. from original position; curvature, 0·8 cm.; distances of bands from membrane, 1·0, 1·3, 1·6, 1·9, 2·4, 3·0, 3·7, 4·8 cm., respectively (see Fig. 1).

After 3 months, the membrane had moved down 2·4 cm.; the bands were very distinct, and composed of coarse, spherical granules in a clear space, the inter-band space being cloudy. After 6 months, the membrane had reached the bottom of the tube, leaving the remains of the bands adhering to the walls (as rings of cloudy gelatinous matter) on pouring out the solution.

Series 3; 10% *solution.* Formation of bands was similar to that in series 2, the bands being closer together and still more solid in texture. After 7 days, 7 bands had formed, and the concave meniscus of the membrane (curvature, 1·0 cm.) actually penetrated the first band. After 14 days, 10 bands were formed, and reached the bottom of the tube; membrane concave; curvature, 0·9 cm.

---

branes were in all cases convex or concave. (*Note.* A water–air meniscus is regarded as concave.)

In measuring the inter-band distances, the bottom of a band was taken, as this was quite definite, whilst the top was practically always diffuse.

FIG. 1.

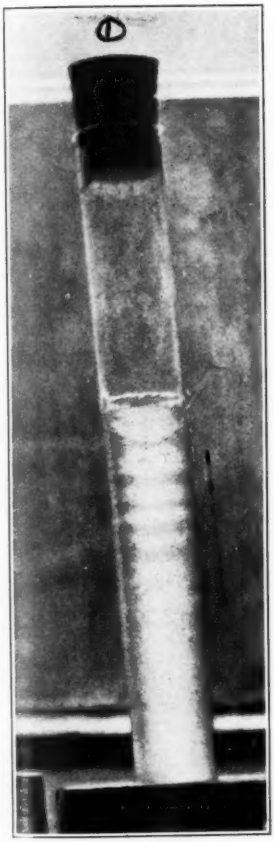
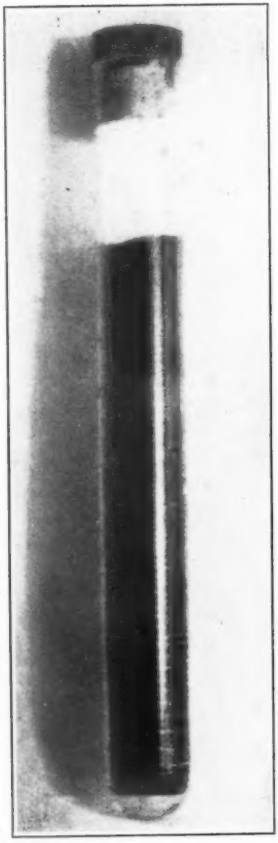


FIG. 2.



[*To face page* 226.]

Series 4; 15% *solution.* Gradual formation of bands, 2 mm. in thickness, and inter-band distance gradually increasing from 1 mm. to 3 mm.

Series 5. *Concentric ring formation with sodium carbonate.* A crystal of sodium carbonate was allowed to penetrate the whole thickness of a set 5% gelatin solution contained in a Petri dish. Concentric rings were formed similar to the bands described above. The same effect was obtained by filling with sodium carbonate solution a cylindrical hole bored through the whole thickness of the gelatin. On the contrary, placing a drop of the sodium carbonate solution on the surface of the gelatin gave no definite rings, the horizontal diffusion not being simultaneous through the whole depth of the gelatin. No bands were obtained on substituting agar-agar for gelatin.

Sodium Hydrogen Carbonate.—The presence of sodium hydrogen carbonate exerted an inhibiting effect on ring formation. The salt itself showed but small tendency to stratification, the bands being few and imperfect.

Sodium Hydroxide (4% *solution*).—The membrane had a concave meniscus, and faint, imperfect bands were formed, a brownish gelatinous precipitate separating.

Barium Hydroxide.—Series 1; 3·5% *solution.* A flat membrane was formed at the junction of the barium hydroxide solution and the gelatin. After 7 days, a cloudy space of about 1 cm. below the membrane was observed, followed by a space of 1·4 cm. occupied by 10 fine rings. After 14 days, the membrane had moved down 2·5 cm., this space being occupied by 25—30 fine bands. Below the membrane a space of 5·0 cm. contained 17 bands. No further change was observed after 21 days.

Series 2; 7% *solution.* After 7 days, the flat membrane had moved down 2·0 cm. from its original position, and above it were very fine, close, film-like bands in two layers: (*a*) upper layer, about 40 equidistant bands occupying 1·8 cm.; and (*b*) lower layer, about 30 equidistant bands, occupying 2·0 cm. Below the membrane was a slightly cloudy region of 2·4 cm. containing 14 distinct bands.

After 14 days, the membrane had moved down 5·4 cm. from its original position, this space being occupied by about 60 bands, the inter-band space increasing from 0·3 mm. to 1·0 mm. towards the membrane. Below the membrane 6 bands were formed, occupying 2·1 cm.

After 21 days, the membrane had reached the bottom of the tube, and below the original position of the membrane the tube was filled with bands, gradually increasing in thickness and distance apart

towards the bottom of the tube. After the contents of the tube had been poured out, the rings adhered to the walls as a white precipitate (see Fig. 2).

The peculiarity of the bands above the membrane, in so far as they differ in appearance and structure from those below, would simply show that they were formed after the passage of the membrane.

Series 3. *Agar-agar medium* (1%). (*a*) Barium hydroxide, 3·5%. A concave membrane was formed, moving down 0·2 cm. in 7 days. A heavy precipitate was found on the membrane, below which was a clearer space of 1·2 cm. followed by a thick band of a distinct yellow colour. Below this the gel was of a green tint.

(*b*) Barium hydroxide, 7·0%. Membrane had moved down 0·1 cm. in 7 days. A very heavy precipitate was on the membrane, below which was a clearer space of 0·3 cm. then one very thick band of yellow colour. Below this, the gel was green.

Ammonium Hydroxide.—Series 1; 5% *solution*. A convex membrane, moving up 1·1 cm. in 7 days, was formed at the junction of the 5% solutions of ammonia and gelatin. This membrane had a rough surface, composed of feathery particles. No bands were observed. After 3 months, the membrane had moved up 5·8 cm., having become flat and indistinct. One band, composed of coarse particles, had appeared 0·3 cm. below the new membrane. The rest of the gel was cloudy. With ammonia solution (*d* 0·880), the diffusion was similar but slower.

Series 2. *Ammonia gas.* Test tubes containing set 5% gelatin solution were filled with ammonia gas and allowed to stand hermetically closed. The gelatin solution liquefied.

Series 3. *Gaseous ammonia–nitrogen mixture.* A 100 c.c. measuring cylinder, containing 75 c.c. of 5% set gelatin solution, was connected to a nitrometer containing a mixture of ammonia gas and nitrogen in the ratio 1 : 3. After 30 minutes, a cloudy membrane was formed, complete liquefaction occurring within 24 hours; the column of liquid presented the appearance of opacity bands, extending throughout the liquid, the band thickness and inter-band distances (equal) being 2·4 cm. (approx.). The opacity bands gradually disappeared, nothing except a general turbidity remaining after 3 hours. On increasing the proportion of ammonia, ordinary liquefaction occurred as in series 2.

Calcium Hydroxide (*Saturated solution*).—A transparent, convex membrane was formed, moving up 0·3 cm. in 14 days. Below the membrane was a cloudy region of 3·2 cm. containing 2 broad bands.

Ring Formation with One Acid.

Series 1; 5% *solution of hydrochloric acid.* A concave membrane composed of fine particles was formed, moving down 3·6 cm. in 7 days. Above the membrane was a cloudy region. As the membrane moved down, faint bands were formed below it. After 3 months, diffusion was complete, the liquid being cloudy. In contrast to those with sodium carbonate, the bands were only of a temporary nature, gradually disappearing. Weaker acid solutions gave no definite bands.

Series 2; 10% *solution.* A concave membrane was formed, moving downwards. After 5 days, very fine translucent bands were formed, slightly resembling the sodium carbonate bands, but farther apart. After 3 months, the diffusion was complete and a white precipitate was at the bottom of the tube. Using 15% and 32% hydrochloric acid, and hydrogen chloride gas (as in the case of ammonia gas) neither membrane nor bands were formed, diffusion increasing with strength of acid.

Experiments with a series of other acids, both organic and inorganic, and also with single salts were carried out, but no definite ring formation was observed. It is noteworthy that, in the majority of cases, inorganic acids gave a concave meniscus moving downwards, whilst organic acids gave a convex one moving upwards.

Bromine Water (*saturated*).—A flat membrane was formed, below which was a thick, opaque mass, followed by a cloudy region. After 11 days, the membrane had moved up 0·8 cm. with an opaque region of 2·1 cm. beneath, and then 2 bands in a cloudy space.

Silver Nitrate (1·7% *solution*).—*In the light.* In place of the ordinary membrane, a dark, wide band was formed. 0·3 Cm. below the first band another wide, dark band was formed, followed by about 2 cm. clear space, and then well-defined bands similar to those in the sodium carbonate experiments.

After 3 months, the membrane band was deep red, and stationary. At the bottom of the tube were 6 distinct bands, 7·6 cm. from the membrane band. A grey deposit on the tube, forming a mirror in places, was seen above the membrane band.

In the dark. Concave membrane.

No bands formed at first. After 14 days, the membrane was still stationary; below it were a dark brown region of 1 cm. and, at the bottom of the tube, faint bands (5 bands in 2·1 cm.).

After 3 months, the membrane was solid and red. The solution was reddish-brown, and the gel red; 7 distinct bands were at the bottom of the tube, 7·0 cm. from the membrane, the intermediate space being clear. No mirror.

No bands were observed on substituting agar-agar for gelatin.

Silver Nitrate and Formaldehyde (0·5% Solution of silver nitrate in 5% gelatin solution, and 40% formaldehyde above).—*In the light.* Membrane reddish-brown, steeply concave, opaque, and 0·2 cm. thick. Beneath the membrane a clear space of 3 cm. with one band. Gelatin below slightly opaque, and reddish-brown.

After 3 months, membrane was steeply concave (0·8 cm.) and 3 bands were seen in the gel, taking the same shape as the membrane.

In the dark. Membrane white, opaque, steeply concave, and 0·1 cm. thick.

Above the membrane was a cloudy layer about 1 cm. thick. No bands of clear space.

After 3 months, the gel was dark brown. No bands or mirror.

Formaldehyde (40% *solution*).—A hard, horny, concave membrane was formed, still stationary after 3 months. The appearance of the gelatin remained unchanged, but on careful examination it was found that its consistency had altered completely, having become hardened throughout in layers. Under the pressure of a glass rod, the layers could easily be distinguished as separated by clear, hard membranes. The gelatinous mass bore a remarkable resemblance to the crystalline lens of an eye. The formaldehyde solution became weaker. Similar results were obtained by employing the 20% solution.

No optical examination could be made of this interesting experiment.

Similar experiments with absolute ethyl alcohol or acetone resulted in the formation of slightly concave, parchment-like, non-permeable membranes. No change was observed after 3 months' keeping.

Section II. (With Hubert Cawood Hillary and Howard Braithwaite Stent.)

Calcium Carbonate and the Liesegang Phenomenon.

As already indicated (J., 1923, **123**, 785), the formation of hydrocalcite ($CaCO_3,5H_2O$) was brought about by forced double decomposition *en masse* of calcium chloride and sodium carbonate. On the other hand, when the interaction was allowed to take a more natural course (*i.e.*, the velocity of reaction was dependent on the rate of diffusion), a series of new and interesting phenomena were observed. To prevent the reaction being instantaneous, advantage was taken of the fact that concentrated solutions of calcium chloride and sodium carbonate differ widely in specific gravity.

On carefully running 600 c.c. of 7% solution of pure sodium carbonate on to 200 c.c. of a 38% solution of pure calcium chloride

contained in a 1000 c.c. glass cylinder, both solutions being at room temperature, a gelatinous semipermeable membrane of hydrocalcite was formed. After 2 hours, the membrane had increased in thickness, the bottom part of the calcium carbonate (the original membrane) showing distinct signs of changing from the translucent gelatinous (hydrocalcite gel) condition to an opaque white crystalline solid (calcite). After 4—5 hours, the membrane had increased in opacity and thickness, showing the solid to be uniformly distributed asbestos-like layers, which in the course of 2 or 3 days spread to a depth of 1·2 cm. Simultaneously with the hardening of the membrane, one or more protuberances or hillocks were observed on the upper layer of the solid. The hillocks soon resembled miniature volcanoes, the eruptions taking the form of fine streamers extending nearly to the surface of the liquid in straight, though not always vertical, chains of gelatinous particles of calcium carbonate. The shot-out streamers, on reaching the surface of the liquid, appeared to bend over and then gradually vanish, giving rise to the remarkable phenomenon of opacity bands or rings, distributed uniformly throughout the upper part of the sodium carbonate solution. In place of the streamers trees began to grow, taking their origin from the protuberances. The trees had the appearance of a wavy, white line or column in a spiral form, the corrugated surface of the column recalling stalagmites or icicles. Not infrequently, the trees were imperfect in their spiral form, being confined almost to one plane. In these cases, the wave maxima invariably coincided with the opacity bands.

After 12—20 hours, the trees extended to the surface of the liquid, often creeping along the walls of the vessel. On nearly reaching the surface, the trees spread into a growth resembling sea plants. This foliage, or calcium carbonate in layers, gradually fell on to the membrane, carrying with it some of the trees, and completely destroying the opacity regions, already disturbed by the growth of the trees. The phenomenon of layers and tree formation persisted apparently indefinitely, provided that experimental conditions remained constant. The trunks of the trees were found to be hollow, a horizontal section of the walls showing concentric rings when magnified.

On long keeping, the bottom part of the laminar membrane gradually broke up and fell to the bottom of the vessel in the form of a fine, crystalline powder of calcite. The edges of the remaining opaque and hardened layers assumed in course of time a zig-zag shape. No appreciable difference was caused by varying the diameter of the vessel or the height of the columns of solution.

On diminishing the concentration of the sodium carbonate, the

whole phenomenon of ring and tree formation became fainter. Reduction of the concentration of the calcium chloride solution, *i.e.*, bringing its specific gravity nearer to that of the sodium carbonate solution, prevented the formation of a membrane and resulted in rapid diffusion.

Experiments were carried out with sodium carbonate and calcium chloride in (*a*) tap water, (*b*) distilled water, (*c*) boiled solution cooled under reduced pressure, (*d*) in the dark, and (*e*) in sunlight; the actual tree growth was unaffected by these modifications of conditions.

Influence of Temperature.—On carrying out the experiments at 0—3°, no tree formation took place, so long as the membrane remained gelatinous. Only on the transformation of the gelatinous membrane (hydrocalcite) to the opaque crystalline layers (calcite), did it become impermeable to diffusion, the force of osmosis breaking through at one or more places of least resistance, forming protuberances, and finally trees. But even at low temperatures some streamers were formed, giving rise to well-defined opacity bands, having a spacing of approximately 0·9 cm. and being ultimately destroyed by the tree formation, on raising the temperature. Above 30°, no Liesegang rings or trees were formed, owing to rapid diffusion and to the fact that at this temperature hydrated calcium carbonate has not even a temporary existence. The semipermeable character of the membrane was well illustrated by colouring the sodium carbonate solution with phenolphthalein or potassium permanganate. In each case, no coloration could be observed below the membrane. Similar results were obtained by colouring the calcium chloride with potassium permanganate.

Calcium Chloride, Sodium Carbonate, and a Colloid.

A narrow 100 c.c. cylinder was half-filled with a 5% solution of gelatin containing 3 g. of calcium chloride per 100 g. of gel. When the gel had set, 50 c.c. of a 15% solution of sodium carbonate were slowly poured on. A whitish membrane was formed, and slow diffusion took place into the gel, causing it to become opalescent. The upper solution remained clear. After 60 hours, the diffusion was complete, the white bands being separated by opalescent spaces speckled with calcium carbonate.

A 1% gel of agar-agar in distilled water, containing 2% of sodium carbonate, with a superimposed 10% solution of calcium chloride gave precipitation of a rhythmic character. With 3% of calcium chloride in the agar-agar gel and 10% sodium carbonate solution above, the precipitation was uniform and slow.

In all cases where gelatin or agar-agar was employed, no streamers,

trees, or opacity bands were observed, the reason probably being that the transition point hydrated—anhydrous calcium carbonate is considerably raised in presence of colloids (compare mother-of-pearl).

Well-defined concentric rings were obtained by fixing a crystal of sodium carbonate in a Petri dish containing set 5% gelatin, with 3% of calcium chloride in solution. The development of the rings was very similar to that described in the case of sodium carbonate (see Section I).

Influence of Light.—As already stated, the access of light influenced the direction of both the trees and the calcium carbonate rings in the gelatin medium. In the experiments on the effect of light on the tree-orientation, vessels 10—13 cm. in diameter were employed. These were entirely covered with black paper, a narrow slit being allowed to remain on the side facing the light. Sunlight, electric and gas lights were tested, the most satisfactory result being given by sunlight. When precautions were taken to prevent vibration and to keep conditions constant, in more than 70% of the cases the trees tended towards the light, regardless of the position of the protuberances. No such relationship could be observed in the case of streamers.

Interesting results were obtained by using vessels (of diameters varying from 3—12 cm.) enclosed in black paper in which small circular apertures were made at various heights of the sodium carbonate column. The light was admitted through a lens, thus focussing it at any particular point in the vessel. It was invariably found that the trees tended towards the focus, so much so that often several of them met in a point, becoming entangled.

In the experiments with a gelatin medium carried out (*a*) in complete darkness, (*b*) in the light, and (*c*) in a vessel covered with black paper, the light being admitted through a narrow slit, the only difference observed between (*a*) and (*b*) was in the velocity of diffusion, the rings being horizontal and equally spaced; in the case of (*c*), the rings, whilst remaining parallel to one another, were inclined towards the light.

Influence of Hydroxy-compounds upon the Colloidal Condition of Calcium Carbonate.—A series of experiments was carried out on lines similar to those described by Neuberg and Rewald (*Biochem. Z.*, 1908, **9**, 547). Both calcium oxide and calcium metal, suspended in absolute ethyl or methyl alcohol, glycerol,* or mixtures of these, gave colloidal calcium carbonate in presence of carbon dioxide. The stability, viscosity, and concentration of the resulting product depended upon the medium and experimental conditions.

* Colloidal calcium carbonate in glycerol may be of therapeutic interest.

Influence of Gelatin upon the Colloidal Condition of Calcium Carbonate.—10 G. of powdered lime were suspended in 200 c.c. of hot 5% gelatin solution. A current of carbon dioxide was passed through for 5 hours, the temperature being allowed to drop to 25°. On keeping, the gelatin solution set to a brownish, opalescent gel, the excess of lime remaining caked at the bottom of the vessel. A white precipitate was thrown down on shaking the gel with water, methyl alcohol, or acetone. Analysis showed the gel to contain 0·67% of calcium carbonate.

No definite results were obtained with agar-agar.

Summary.

(1) The Liesegang phenomenon is a material record of a periodic function, *viz.*, the action of a single substance upon a mobile medium, capable of undergoing either structural deformation or systematic orientation. Such a medium may be a colloid or finely-divided suspended matter. The substance is, as a rule, sufficiently strongly acidic or basic to cause a physical change in the medium. The suitable character of the substance and the condition of the medium may be developed *in situ*.

(2) Opacity bands and tree formation are special cases of the Liesegang phenomenon, the former being produced under very mild experimental conditions, and the latter under the influence of forced irregular diffusion.

THE UNIVERSITY, MANCHESTER. [*Received, September 11th*, 1924.]

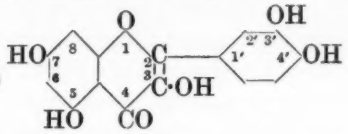
XXXVI.—*The Position of the Sugar Nucleus in the* Quercetin *Glucosides.*

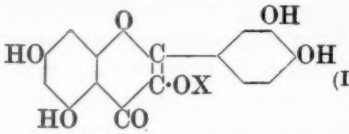
By GORDON FREDERICK ATTREE and ARTHUR GEORGE PERKIN.

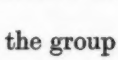
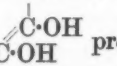
A KNOWLEDGE of the position of the sugar nucleus in the flavonol glucosides is of special interest, on account of the inter-relationship between these compounds and the naturally occurring anthocyanins. From an examination of the dyeing properties of the hydroxyflavone and -flavonol colouring matters, especially towards aluminium and tin mordants, it has been possible to estimate the tinctorial effect of each of the hydroxyls present in these compounds and thus to predict to some extent the position of the sugar nucleus in their glucosides.

It is now known in regard to quercetin (I) that three factors influence its dyeing property in this respect: (*a*) the hydroxyls 5 and 7, the effect of which is almost negligible (pale yellow); (*b*) the hydroxyls 3′ and 4′, which jointly are powerful auxochromes

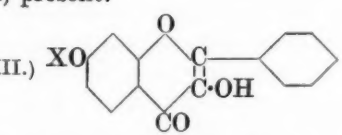
(deep yellow); and (*c*) the hydroxyl 3, which itself creates dyeing property (pale yellow) and enhances that given by (*b*) to deep orange.

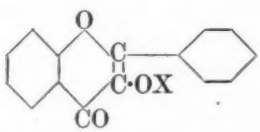
(I.) 

 (II.)

Interesting again is the fact that the pale yellow shade due to hydroxyl 3 is much strengthened by the presence of hydroxyl 7 or 4′, and if *p*-quinonoid formulæ are adopted, this effect may be assumed to originate in the group  or  present.

Mainly from these considerations, it was predicted (J., 1899, **75**, 826; 1902, **81**, 589) that as quercitrin gives yellow tones, the rhamnose nucleus present therein will be in union with either the 3- or the 3′-hydroxyl group, and of these, the former suggestion (II) is now known to be correct. Thus, by the action of diazomethane on quercitrin, Herzig and Schönbach (*Monatsh.*, 1912, **33**, 678) obtained a crude quercitrin pentamethyl ether, which when hydrolysed gave the 5 : 7 : 3′ : 4′-tetramethoxyflavonol previously synthesised by v. Kostanecki, Lampe, and Tambor (*Ber.*, 1904, **37**, 1402), thus indicating that the rhamnose nucleus is present in the 3-position. More recently, Shibata and Kimotsuki (*Acta Phytochim*, 1923, **1**, 91) have studied the ultra-violet absorption spectra of hydroxy-flavones and -flavonols, and find that by this method it is possible to distinguish the one from the other. Tasaki (*ibid.*, 1925, **2**, 129) has similarly examined the hydroxy-flavone and -flavonol glucosides and as a result considers that these fall into the groups (III) and (IV) in regard to the position of the sugar group (X) present.

(III.) 

 (IV.)

In group (III) occur the flavone glucosides, and rutin, whereas in group (IV) are placed the flavonol compounds, robinin, kæmpferitrin, quercitrin, and myricitrin. Such a formulation (IV) is in full agreement with the dyeing properties of the latter, and is certainly correct in regard to quercitrin (*loc. cit.*).

On the other hand, the inclusion of the quercetin glucoside rutin in group (III) does not harmonise with the tinctorial behaviour of this compound.

The experiments herein described are concerned with the methyl-

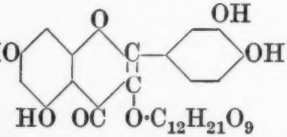
ation of rutin, xanthorhamnin, *iso*quercitrin, and quercimeritrin with diazomethane, and have clearly indicated the position of the sugar group in these glucosides.

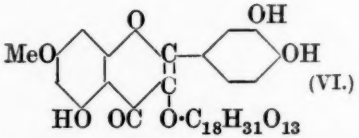
The rutin employed was obtained from the leaves of the *Eucalyptus macrorhyncha* (Smith, J., 1898, **73**, 697; Perkin, J., 1902, **81**, 478) and yielded with diazomethane a dull orange resin, $C_{27}H_{25}O_{11}(OMe)_5$.

Although ter Meulen (*Rec. trav. chim.*, 1923, **42**, 280) has stated that rutin is $C_{33}H_{42}O_{20},4H_2O$ and is derived from quercetin and the trisaccharide rhamninose, Charaux (*Compt. rend.*, 1924, **178**, 1312) finds that the older formula $C_{27}H_{30}O_{16}$ is in reality correct and that the sugar group present therein is the disaccharide rutinose.

When hydrolysed with dilute acid, rutin pentamethyl ether gave 5 : 7 : 3′ : 4′-tetramethoxyflavonol, the identity of which was confirmed by comparison with a specimen derived from quercitrin according to the directions of Herzig and Schönbach (*loc. cit.*). Rutin thus possesses the formula (V), and the statement of Tasaki that the sugar nucleus of this glucoside is present in the 7-position is therefore incorrect.

(V.)





(VI.)

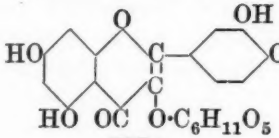
Although it is usually possible to ascertain the positions of the methoxy-groups in methoxy-flavones and -flavonols by means of alcoholic potash, at 170° 5 : 7 : 3′ : 4′-tetramethoxyflavonol is but little attacked in this manner, owing most likely to the sparing solubility of its potassium salt. After some hours at 200°, small amounts of phloroglucinol monomethyl ether and veratric acid were produced, but the presence of phloroglucinol dimethyl ether could not be detected. It is thus probable that at the high temperature involved, a preliminary conversion of the 5 : 7 : 3′ : 4′-tetramethoxyflavonol into the 5-hydroxy-7 : 3′ : 4′-trimethoxy-compound takes place, and that this then suffers hydrolysis as indicated above.

Xanthorhamnin, $C_{34}H_{42}O_{20}$, a yellow-dyeing glucoside obtained from Persian berries, consists of rhamnetin (quercetin 3-monomethyl ether) in union with the trisaccharide rhamninose (Tanret, *Compt. rend.*, 1899, **129**, 725). This, with excess of diazomethane, gave a yellowish-brown resin, which by hydrolysis with acid yielded similarly to quercitrin and rutin the 5 : 7 : 3′ : 4′-tetramethoxy-flavonol. Xanthorhamnin thus has the structure (VI). When less diazomethane is employed, a methylation product can be isolated

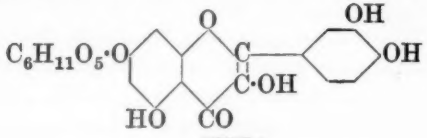
as pale yellow needles, which approximates in composition to a xanthorhamnin trimethyl ether, $C_{34}H_{39}O_{17}(OMe)_3,3H_2O$. Hydrolysis gave yellow needles consisting mainly of a quercetin trimethyl ether, evidently the 7 : 3′ : 4′-compound, but containing a trace of the 5 : 7 : 3′ : 4′-tetramethoxyflavonol.

iso*Quercitrin*, $C_{21}H_{20}O_{10}$, which consists of quercetin in union with glucose, is present in cotton flowers (Perkin, J., 1909, **95**, 2190) and in brown husked maize (Sando and Bartlett, *J. Biol. Chem.*, 1922, **54**, 636).

The small amount available gave with diazomethane pale yellow, flat needles of a methylated glucoside, m. p. 150—152°, and from this by hydrolysis 5 : 7 : 3′ : 4′-tetramethoxyflavonol was produced. *iso*Quercitrin (VII) is thus analogous to rutin and xanthorhamnin.



(VII.)



(VIII.)

Quercimeritrin, $C_{21}H_{20}O_{12}$, occurs in cotton flowers (Perkin, *loc. cit.*), in *Prunus emarginata* (Finnemore, *Pharm. J.*, 1910, **31**, 604), and in *Helianthus annuus* (Sando, *J. Biol. Chem.*, 1925, **64**, 74).

It differs from the yellow-dyeing *iso*quercitrin in giving orange shades similar to those obtained from quercetin itself, and mainly on this account was considered most probably to possess the formula (VIII) (Perkin, *loc. cit.*). With diazomethane, it gave almost colourless needles, m. p. 203—205°, sintering at 197°, which there is little doubt consist of the pentamethyl ether, $C_{21}H_{15}O_7(OMe)_5,2H_2O$. By hydrolysis, colourless needles of a sparingly soluble quercetin tetramethyl ether, m. p. 284—285°, were obtained, the acetyl derivative of which melts at 174—176°. As this, when digested with alcoholic potash at 180°, readily gives veratric acid and phloroglucinol monomethyl ether, it is evidently the hitherto unknown 5 : 3 : 3′ : 4′-tetramethoxy-compound. Thus of the five possible quercetin tetramethyl ethers, three only can give veratric acid. These are now known, and as the 7 : 3 : 3′ : 4′- and the 5 : 7 : 3′ : 4′-compounds melt respectively at 156—157° and 195—198°, the quercetin tetramethyl ether derived from quercimeritrin must possess the constitution here stated. Quercimeritrin therefore has the formula (VIII), which, as already suggested, is in harmony with its dyeing properties.

Of the five known quercetin glucosides, therefore, four contain the sugar group in union with the pyrone hydroxyl, and if, as appears likely (compare Tasaki), kæmpferitrin, robinin, and myricitrin are

analogously constituted, quercimeritrin will be the only known flavonol glucoside which differs in this respect.

Experimental.

Rutin (2 g.) in methyl alcohol (30 c.c.) was treated with diazomethane prepared from nitrosomethylurethane (8 c.c.) in ether (80 c.c.) and 25% methyl-alcoholic potash (25 c.c.); precipitation of the rutin by the ether was prevented by additions of methyl alcohol (5 c.c.) from time to time (compare Herzig and Schönbach, *loc. cit.*). On the following day, the solution was again treated as before with diazomethane; then, after 48 hours, it was concentrated, diluted with boiling water to remove the last traces of alcohol, and evaporated to dryness (Found: CH_3, 11·4. Rutin pentamethyl ether, $C_{32}H_{40}O_{16}$, requires CH_3, 11·0%). The yellowish-brown resin was digested with boiling 0·5% sulphuric acid (200 c.c.) for 2 hours, yielding a precipitate which crystallised from benzene in colourless needles; these, alone or mixed with 5 : 7 : 3′ : 4′-tetramethoxyflavonol prepared from quercitrin by Herzig and Schönbach's method, melted at 194—196° (Found: C, 63·6; H, 5·1; CH_3, 16·5. Calc. for $C_{19}H_{18}O_7$: C, 63·7; H, 5·1; CH_3, 16·75%). The acetyl derivative melted at 160—162° (Herzig and Schönbach give m. p. 160—163°).

Xanthorhamnin (2 g.) in methyl alcohol (50 c.c.) was treated with diazomethane as in the case of rutin; after being kept over-night, the liquid, containing crystals in suspension (A), was evaporated to half its volume, and again treated with diazomethane from nitrosomethylurethane (4 c.c.). The solution was evaporated to dryness and the residue digested with boiling 0·5% sulphuric acid (100 c.c.). The precipitate obtained crystallised from benzene in colourless needles, m. p. 194—196°, and, admixed with the 5 : 7 : 3′ : 4′-tetramethoxyflavonol derived from rutin, showed no alteration in melting point.

If the mixture (A) was evaporated to half its volume and kept, fine, colourless needles (1·7 g.) separated. These melted at 175—178° (those from a second experiment at 172—178°), became yellow when dried over sulphuric acid, were readily soluble in water, and gave with ferric chloride a brown coloration (Found: H_2O at 140°, 6·7; CH_3, 6·8. Xanthorhamnin trimethyl ether, $C_{37}H_{48}O_{20},3H_2O$, requires H_2O, 6·2; CH_3, 6·8%). On hydrolysis with boiling 1% sulphuric acid, fine, yellow needles separated which, after recrystallisation from alcohol, melted at 170—172° (Found: CH_3, 14·1. $C_{18}H_{16}O_7$ requires CH_3, 13·1%). It was evidently quercetin 7 : 3′ : 4′-trimethyl ether (rhamnetin dimethyl ether) contaminated with a small amount of the 5 : 7 : 3′ : 4′-tetramethoxy-compound.

iso*Quercitrin* (0·6 g.) in methyl alcohol was treated with diazomethane from nitrosomethylurethane (4 c.c.); crystals separated over-night. The ether was distilled off, and the liquid again treated with diazomethane as before. Pale yellow needles slowly separated (0·4 g.) which sintered slightly at 140° and melted at 150—152°. This compound, on hydrolysis with boiling 1% sulphuric acid, gave needles which, after recrystallisation from benzene, melted at 193—195°, and, as a mixed melting-point determination showed, consisted of 5 : 7 : 3′ : 4′-tetramethoxyflavonol.

Quercimeritrin (2 g.) in methyl alcohol (80 c.c.) was methylated with ethereal diazomethane from nitrosomethylurethane (8 c.c.), methyl alcohol (20 c.c.) being added gradually at the same time. On the following day, the ether was removed by distillation, methyl alcohol (50 c.c.) added, and the solution again treated with the same amount of diazomethane. When the latter proved to be absent, the liquid was evaporated to a small bulk and diluted with a few drops of water; almost colourless needles (1 g.) then slowly separated. These sintered at 197°, melted at 203—205°, and could be recrystallised from water. With ferric chloride solution, no coloration was produced, indicating complete methylation (Found :* C, 54·05; H, 6·0; H_2O, 6·7. $C_{26}H_{30}O_{12},2H_2O$ requires C, 54·7; H, 6·0; H_2O, 6·3%). This compound, apparently quercimeritrin pentamethyl ether, on hydrolysis (1 g.) with boiling 1% sulphuric acid for 4 hours, gave a semi-gelatinous precipitate (0·635 g.). It was dissolved in much boiling alcohol in presence of animal charcoal, and the solution evaporated until crystallisation commenced. The fine, colourless needles obtained were evidently pure, as the melting point, 284—285°, was unaltered after recrystallisation (Found:* C, 63·6; H, 5·1. $C_{19}H_{18}O_7$ requires C, 63·7; H, 5·0%).

This new *quercetin tetramethyl ether*, which is very sparingly soluble in alcohol, dissolves in alkaline solutions with a pale yellow colour. The *acetyl* derivative forms minute, colourless needles, m. p. 174—176° (Found :* C, 62·8; H, 5·3; CH_3, 14·2. $C_{21}H_{20}O_8$ requires C, 63·0; H, 5·0; CH_3, 15·0%). In order to determine the positions of the methoxy-groups, the tetramethyl ether (0·6 g.) in 20% alcoholic potash (5 c.c.) and water (1 c.c.) was heated at 170—180° for 3 hours. The pale yellow liquid was evaporated to dryness, the residue dissolved in water, and the solution saturated with carbon dioxide. Extraction with ether removed a colourless, viscid product, the solution of which in dilute aqueous sodium carbonate was treated with benzenediazonium chloride. The orange-red precipitate was dried and extracted with a little alcohol, and the residue was crystallised from alcohol–acetic acid. The crystals, m. p. 250—252°, evidently consisted of benzeneazophloro-

glucinol monomethyl ether. Addition of acid to the bicarbonate solution remaining after the extraction with ether gave a deposit of veratric acid, m. p. 174—176°. The quercetin methyl ether, m. p. 284—285°, derived, as above stated, from quercimeritrin, is accordingly 5 : 3 : 3′ : 4′-tetramethoxyflavonol.

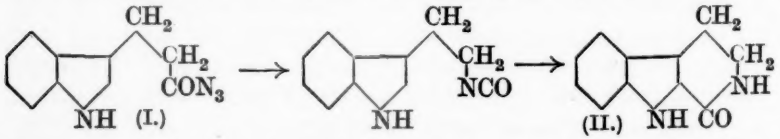
We are greatly indebted to Mr. Arthur Bennett of the Chemistry Department of the University of Manchester for the numerous microanalyses (marked*) which he has carried out in connexion with this work, and we desire to acknowledge a grant from the Department of Scientific and Industrial Research which enabled one of us (G. F. A.) to take part in this investigation.

Clothworkers Research Laboratory,
The University, Leeds. [*Received, November 29th*, 1926.]

XXXVII.—*The Decomposition of β-3-Indolylpropionic Azide.*

By Richard Helmuth Fred Manske and Robert Robinson.

In a recent synthesis of harmaline (Manske, Perkin, and Robinson, this vol., p. 1) advantage was taken of the Japp-Klingemann reaction for the preparation of arylhydrazones of certain α-diketones and α-keto-acids. In continuation of the work, an attempt was made to obtain 3-β-aminoethylindole by applying the Curtius reaction to β-3-indolylpropionic acid. A remarkably satisfactory method of preparation of this acid was devised, but the same process has quite recently (*Ber.*, 1926, **59**, 1858) been placed on record by Kalb, Schweitzer, and Schimpf, so that a detailed description is unnecessary; the chief variations are mentioned in the experimental section. Methyl β-3-indolylpropionate was converted in the normal manner into the related hydrazide and azide (I). The nature of the products obtained on the decomposition of the latter substance varies with the conditions, and in benzene solution, in presence of hydrogen chloride, the carbimide, which is doubtless initially formed, undergoes intramolecular con-

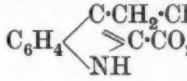


densation with the formation of 3-keto-3 : 4 : 5 : 6-tetrahydro-4-carboline (II). The constitution of the product is proved by the fact that on distillation with zinc dust in a stream of hydrogen

it gives a small amount of norharman along with indole. The reaction involved is analogous to that occurring in the formation of *iso*quinoline by dehydration of cinnamaldoxime.

EXPERIMENTAL.

Ethyl β-2-*Carbethoxy*-3-*indolylpropionate*,



—The following process gives excellent results, but it is essential to avoid needless delays. A benzenediazonium chloride solution is prepared from aniline (38 g.), concentrated hydrochloric acid (100 c.c.), sodium nitrite (28 g.), and ice (200 g.); potassium hydroxide (48 g.) is dissolved in water (600 c.c.). One-half of the latter solution is shaken in a separator with ethyl *cyclo*pentanone-carboxylate (63 g.) and a small volume of undissolved oil is taken up in benzene. The aqueous layer is added to crushed ice (400 g.), and the benzene layer shaken with the remainder of the alkali. About half the diazo-solution is then added to the solution of the ester and after a minute the remainder of the alkali is introduced from the tap funnel, followed by the second half of the diazo-solution. After 5 minutes, the solution is acidified with concentrated hydrochloric acid (100 c.c.) and the precipitated mass is washed by decantation and dried. This crude phenylhydrazone of ethyl hydrogen α-ketoadipate (55·6 g.) is refluxed with 98% alcohol (156 c.c.) and concentrated sulphuric acid (40 g.) for 2·5 hours. On addition of water, cooling, and washing with sodium hydrogen carbonate solution, the product is obtained in a granular form. It is dried and purified by distillation in a high vacuum; b. p. 212°/2 mm. (yield, 43 g.; m. p. 94°). The ester crystallises from benzene in large, colourless prisms, m. p. 95—96°. The results of elementary analysis of this ester, the dicarboxylic acid obtained on hydrolysis, and the indolepropionic acid derived by heating the dibasic acid were in satisfactory agreement with theory. *Methyl* β-3-*indolylpropionate* crystallises from methyl alcohol in prisms, m. p. 79—80° (Found: N, 7·1. $C_{12}H_{13}O_2N$ requires N, 6·9%).

β-3-*Indolylpropionhydrazide*, $C_6H_4{:}C_2H_2N{\cdot}C_2H_4{\cdot}CO{\cdot}N_2H_3$, was prepared by the interaction of the methyl ester (40 g.) and hydrazine hydrate (15 g.) (oil-bath at 140°); the product (yield, 39 g.) crystallised from alcohol in colourless, hexagonal prisms or tablets, m. p. 129—130° (Found: N, 19·9, 20·4. $C_{11}H_{13}ON_3$ requires N, 20·8%). This hydrazide is sparingly soluble in cold alcohol and moderately readily soluble in hot water.

3-Keto-3 : 4 : 5 : 6-tetrahydro-4-carboline (II).—Crushed ice (200 g.) was added to a solution of β-3-indolylpropionhydrazide (10 g.) in acetic acid (50 c.c.), and sodium nitrite (4 g.) dissolved in a little water was then introduced. The liquid became milky, and in a few minutes pasty, owing to the separation of the crystalline azide (I). This was collected, washed with water, and drained as far as possible; it was then gradually added to boiling benzene (75 c.c.). Nitrogen was evolved and when this stage was completed a stream of hydrogen chloride was led through the hot solution. The benzene was finally distilled, and the residue washed with dilute hydrochloric acid. The substance (yield, 6—7 g.) crystallises from alcohol (charcoal) in characteristic, colourless, spear-head-shaped, microscopic prisms, m. p. 173—174° (Found: C, 71·1; H, 5·4; N, 15·1. $C_{11}H_{10}ON_2$ requires C, 70·9; H, 5·4; N, 15·0%). This cyclic amide is sparingly soluble in cold alcohol or ether and is readily soluble in hot alcohol. It dissolves in warm concentrated hydrochloric acid, but is precipitated on the addition of water; no indole colour reactions are exhibited. On distillation with zinc dust in a stream of hydrogen the chief product was a neutral compound having the properties of indole, but by extraction of the distillate with dilute hydrochloric acid a small quantity of norharman was obtained. The base was recognised by its appearance and m. p. (198°), and by the blue fluorescence of its aqueous acid solutions.

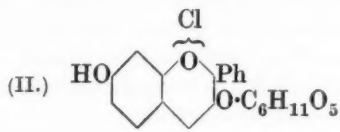
THE UNIVERSITY, MANCHESTER. [*Received, December 10th*, 1926.]

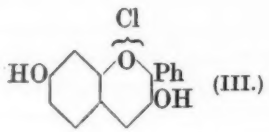
XXXVIII.—*Experiments on the Synthesis of Anthocyanins. Part II. The Synthesis of 3- and 7-Glucosidoxyflavylium Salts.*

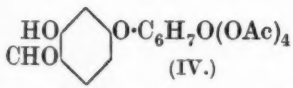
By ALEXANDER ROBERTSON and ROBERT ROBINSON.

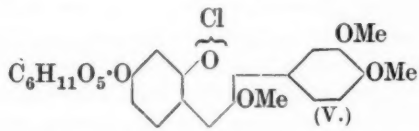
IN the first part of this series (J., 1926, 1713) it was shown that certain glucosides of pyrylium salts of anthocyanidin type may be prepared by relatively simple applications of the general method. In these cases, however, the carbohydrate group was associated with the position 4′ in the flavylium nucleus, whereas in the natural anthocyanins the available evidence shows that the sugar is attached to one of the positions 3, 5, and 7. Thus Willstätter and his collaborators found that all the anthocyanins derived from cyanidin gave a strong ferric chloride reaction and hence bear hydroxyl groups in positions 3′ and 4′. We have accordingly carried our investigation to a further stage by applying the processes already developed to the synthesis of flavylium salt glucosides which should,

in respect of the position of the glucose residues, be more closely allied to the anthocyanins than any as yet obtained. ω-O-*Tetra-acetylglucosidoxyacetophenone*, $Ph{\cdot}CO{\cdot}CH_2{\cdot}O{\cdot}C_6H_7O(OAc)_4$ (I), prepared from benzoylcarbinol and tetra-acetylglucosidyl bromide with the help of silver carbonate, condensed with β-resorcylaldehyde in ethereal solution in presence of hydrogen chloride to a product which was not crystallised but was at once hydrolysed by means of methyl-alcoholic ammonia. The recovered pyrylium salt was difficult to purify, but, ultimately, 3-β-*glucosidoxy*-7-*hydroxyflavylium chloride* (II) was isolated. On hydrolysis, this yielded glucose and 3 : 7-dihydroxyflavylium chloride (III), which has also been obtained by a direct condensation of β-resorcylaldehyde and benzoylcarbinol, or its acetate. The salt has been previously obtained by demethylation of its 3-methyl ether (Pratt and Robinson, J., 1924, **125**, 191).









Similarly, the *tetra-acetylglucoside* (IV) has been prepared by the interaction of β-resorcylaldehyde and tetra-acetylglucosidyl bromide in acetone solution in presence of aqueous potassium hydroxide; in this case, condensation with ω-methoxyacetoveratrone was effected. The resulting flavylium chloride was deacetylated in the usual manner and 7-*glucosidoxy*-3 : 3′ : 4′-*trimethoxyflavylium chloride* (V) was then isolated in a satisfactory condition of purity. On boiling with hydrochloric acid, the glucose was detached and fisetinidin chloride trimethyl ether (Pratt and Robinson, J., 1925, **127**, 170) was obtained.

Experimental.

ω-O-*Tetra-acetyl*-β-*glucosidoxyacetophenone* (I).—Freshly-precipitated silver carbonate (6 g.) was added to a solution of *O*-tetra-acetyl-α-glucosidyl bromide * (6 g.) and anhydrous benzoyl-

* Hudson (*J. Amer. Chem. Soc.*, 1924, **46**, 466, 979, 2501) indicated that this substance, the so-called acetobromoglucose, is probably an α-glucose derivative and yields β-glucosides through a Walden inversion.

carbinol * (5 g.) in dry ether (70 c.c.), which was then gently refluxed for 14 hours. The filtered solution was freed from ether under diminished pressure, a solution of the syrupy residue in acetone (50 c.c.) poured in a fine stream into cold water, and the precipitated viscous mass triturated with fresh water until it crystallised. The dried material was crystallised several times from 86% methyl alcohol (charcoal) and finally obtained in white, prismatic needles, m. p. 104—105° (yield of pure product, 4 g.) (Found: C, 56·4; H, 5·7. $C_{22}H_{26}O_{11}$ requires C, 56·6; H, 5·6%). The substance is moderately readily soluble in cold methyl or ethyl alcohol and is easily soluble in the hot solvents. At room temperature, 100 c.c. of dry ether dissolve about 1·2 g. of the glucoside. The condensation may also be effected in the cold and without a solvent and, though the process is slower than that described above, the yield is about the same.

3-β-*Glucosidoxy*-7-*hydroxyflavylium Chloride* (II).—Condensation of tetra-acetylglucosidoxyacetophenone and β-resorcylaldehyde in presence of hydrogen chloride occurs in absolute formic acid solution, but the product is contaminated with the sugar-free pyrylium salt. Trials showed, however, that in ethereal solution the hydrolysis of the glucoside does not occur in 96 hours, although in this case the reaction is very sluggish. A cooled solution of tetra-acetylglucosidoxyacetophenone (1 g.) and β-resorcylaldehyde (1·5 g.) in dry ether (100 c.c.) was saturated with hydrogen chloride and allowed to remain for 96 hours. The dark brown, viscous mass obtained on the addition of light petroleum was separated, washed with ether, and dried in a vacuum; it became a brittle solid which could not be crystallised. Deacetylation was effected by means of saturated methyl-alcoholic ammonia at 0° during 14—15 hours, the ammonia and methyl alcohol being then removed below 25° under diminished pressure. The residue was dissolved in 2% methyl-alcoholic hydrogen chloride (40 c.c.), and the glucoside precipitated from the filtered solution by the addition of ether (300 c.c.). The amorphous products from several experiments were combined and dried in a vacuum. A mixture of the crude material (4 g.), methyl alcohol (50 c.c.), and 12% hydrochloric acid (5 c.c.) was heated to the boiling point for 1 minute, a large proportion of the impurities being thus dissolved, and filtered hot.

* Benzoylcarbinol was prepared by the method of O. Fischer and Busch (*Ber.*, 1891, **24**, 2680) from ω-bromoacetophenone, the yield being 80%. The hydroxyketone was not, however, isolated by means of ether, but was separated from an aqueous solution by the addition of potassium carbonate. It was dehydrated by distillation of a solution in a large volume of benzene and finally crystallised from light petroleum in glistening plates, m. p. 85—86°.

The orange-red residue was easily soluble in 2% hydrochloric acid and in 2% methyl-alcoholic hydrogen chloride. The glucoside (2 g.) was dissolved in a hot mixture of methyl alcohol (15 c.c.) and 2% hydrochloric acid (10 c.c.), and the filtered solution allowed to remain for 24 hours. Most of the alcohol evaporated and crystals were deposited; the process was thrice repeated, and the salt obtained in bundles of microscopic, pointed rods which matted together on the filter and when dry exhibited a golden reflex. The salt was dried for 3 hours, powdered, and again dried in a vacuum for 15 hours (Found: C, 56·6; H, 5·0; Cl, 8·2, 7·8. $C_{21}H_{21}O_8Cl,0{\cdot}5H_2O$ requires C, 56·6; H, 4·9; Cl, 8·0%). The substance is readily soluble in 2% and 4% hydrochloric acid and in the simple alcohols to orange solutions which become red on the addition of sodium acetate. Pseudo-base formation was observed and the salt is only partly extracted from an aqueous acid solution by means of *iso*amyl alcohol. On boiling with 15% hydrochloric acid for 5 minutes, hydrolysis occurred and, after cooling, 3 : 7-dihydroxyflavylium chloride separated from the solution in orange-brown prisms. The salt was identified by comparison with an authentic specimen.

3 : 7-*Dihydroxyflavylium Chloride* (III).—(A). A solution of β-resorcylaldehyde (1·0 g.) and ω-acetoxyacetophenone (1·2 g.) in formic acid (20 c.c.) was saturated with hydrogen chloride. A week later, the crude product was isolated after precipitation by ether and boiled with 0·2% hydrochloric acid, and the solution filtered. Concentrated hydrochloric acid was then added, bringing the acid concentration to about 8%, and, on cooling, the salt crystallised in deep orange-brown, elongated, rhombic, pointed prisms (yield, 0·3 g.) (Found in material dried in a vacuum: C, 61·6; H, 4·4. Calc. for $C_{15}H_{11}O_3Cl,H_2O$: C, 61·5; H, 4·5%).

(B). The condensation of β-resorcylaldehyde (0·5 g.) and benzoylcarbinol (0·5 g.) in formic acid (20 c.c.) by means of hydrogen chloride occupied 72 hours and the yield of the pure salt was 0·35 g., about twice as great as that obtained from ω-acetoxyacetophenone. The properties of the salt were in agreement with those described by Pratt and Robinson (*loc. cit.*).

4-*O*-*Tetra-acetylglucosidoxy*-2-*hydroxybenzaldehyde* (IV).—A solution of potassium hydroxide (2·6 g.) in water (25 c.c.) cooled to 10° was gradually added to one of β-resorcylaldehyde (6 g.) and *O*-tetra-acetylglucosidyl bromide (18 g.) in pure acetone (55 c.c.), the temperature being maintained below 16° by cooling in ice-water. Two layers appeared and, after 30 minutes, acetone (20 c.c.) was added and the homogeneous solution was allowed to remain for 12 hours. The liquid was rendered faintly acid by the addition of

a little dilute acetic acid, and the acetone removed in a vacuum below 25°. The thick residual syrup, which became semi-solid on trituration with cold water, was several times crystallised (charcoal) from 85% methyl alcohol; it was finally obtained in almost colourless, silky, prismatic needles, m. p. 134—135° (Found: C, 53·5; H, 5·1. $C_{21}H_{24}O_{12}$ requires C, 53·8; H, 5·1%). (A mixture with β-resorcylaldehyde, also m. p. 135°, had m. p. 90—100°.) This acetylglucoside is moderately readily soluble in methyl or ethyl alcohol, sparingly soluble in cold 85% methyl alcohol, and very readily soluble in hot alcohol. 100 C.c. of dry ether dissolve about 1 g. at room temperature. Ferric chloride added to an alcoholic solution gives a dark red coloration identical with that developed by 2-hydroxy-4-methoxybenzaldehyde under similar conditions. The residues from this preparation were examined, but an isomeric compound could not be isolated.

7-*Glucosidoxy*-3 : 3′ : 4′-*trimethoxyflavylium Chloride* (V).—A solution of tetra-acetylglucosidoxyhydroxybenzaldehyde (2 g.) and ω-methoxyacetoveratrone (3 g., an excess) in dry ether (200 c.c.) was saturated with hydrogen chloride at 16—18° and allowed to remain for 72 hours. Almost the whole of the product crystallised in compact clusters of slender, prismatic needles which were dark brown in mass (yield, 2 g.). Recrystallisation from 0·5% hydrochloric acid could not be satisfactorily accomplished owing to the tendency of the substance to give a crystalline, colourless pseudobase, whilst with more concentrated acid deacetylation appeared to occur; moreover, in 2% to 4% hydrochloric acid the salt was only sparingly soluble to an orange-red solution. A solution of the acetylglucoside (2 g.) in methyl alcohol (150 c.c.) was saturated at 0° with ammonia and allowed to remain at 0° for 14 hours; the ammonia and methyl alcohol were then removed under diminished pressure and below 20° until the volume was about 15 c.c. Hydrochloric acid (30 c.c. of 4%) at 50° was added and, on cooling, the chloride separated in crimson, rhombic plates (yield, 1·5 g.) which exhibited a brilliant golden reflex. Recrystallisation in a similar form was effected by dissolving 1 g. in hot methyl alcohol (15 c.c.), adding warm 4% hydrochloric acid (30 c.c.), heating the mixture to 60—70° (it must not be boiled) and filtering it. The salt was dried in a high vacuum for 48 hours (Found: C, 54·2; H, 5·7; Cl, 6·7. $C_{24}H_{27}O_{10}Cl,H_2O$ requires C, 54·5; H, 5·5; Cl, 6·8%). Concentrated acid solutions are crimson and dilute solutions are orange-red. This glucoside is readily hydrolysed, even by 4% hydrochloric acid, and on being treated in the usual way with boiling 15% hydrochloric acid it yielded fisetinidin chloride trimethyl ether, which was identified by comparison with an authentic specimen (Pratt

and Robinson, *loc. cit.*). The *picrate* of the glucoside separated from a warm alcoholic solution of the chloride and picric acid in fine needles and crystallised from 85% ethyl alcohol, containing a little picric acid, in balls of bright red, very slender, prismatic needles which filled the liquid. On heating, decomposition commenced at 240—243° and was complete at 250—252°. In contrast, the acetylated glucoside did not yield a stable picrate.

We desire to thank the International Education Board of New York for a Fellowship which has enabled one of us to take part in the investigation, and the Government Grant Committee of the Royal Society for a grant which has defrayed a part of the expense of the work.

THE UNIVERSITY, MANCHESTER. [*Received, December 10th*, 1926.]

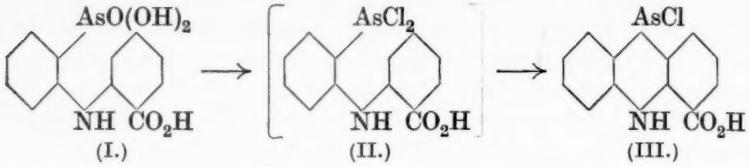
XXXIX.—10-*Chloro*-5 : 10-*dihydrophenarsazine and its Derivatives. Part IV. Carboxy-derivatives.*

By HAROLD BURTON and CHARLES STANLEY GIBSON.

APART from the synthesis of 10-chloro-5 : 10-dihydrophenarsazine (J., 1926, 452), the parent substance and all its analogues so far described have been prepared by the action of arsenious chloride on diphenylamine and its analogues, respectively (*ibid.*, pp. 450, 464, 2241, where all references are given). Owing to the difficulty of obtaining diphenylaminomonocarboxylic acids, carboxy-derivatives of 10-chloro-5 : 10-dihydrophenarsazine could not be obtained directly and it was necessary to study the condensation of *o*-bromophenylarsinic acid with different aminobenzoic acids.

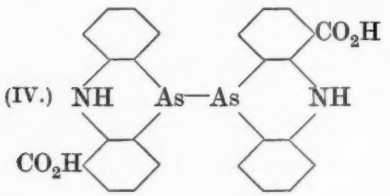
Anthranilic acid condenses readily with *o*-bromophenylarsinic acid in boiling nitrobenzene in presence of anhydrous potassium carbonate and a small quantity of copper powder, forming 2-*carboxydiphenylamine*-6′-*arsinic acid* (I). This acid, on reduction with sulphur dioxide in alcoholic-hydrochloric acid solution, is readily converted into 2-*carboxydiphenylamine*-6′-*arsenic dichloride* (II), which, however, cannot be isolated in the pure condition owing to the ease with which it loses hydrogen chloride. Complete conversion of this compound into 10-*chloro*-5 : 10-*dihydrophenarsazine*-4-*carboxylic acid* (III) can be accomplished either by boiling the acetic acid solution of the reduction product or by dissolving the latter in hot sodium hydroxide solution, boiling for a few minutes,

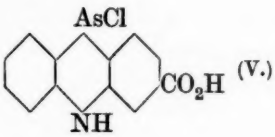
and then precipitating the final product by the addition of an excess of concentrated hydrochloric acid.



(I.) (II.) (III.)

Whilst its solubility in neutral solvents is much less, as far as its chemical properties are concerned, 10-chloro-5 : 10-dihydrophenarsazine-4-carboxylic acid is very similar to the parent compound. When reduced with hypophosphorous acid, it yields a cacodyl derivative, *viz.*, 10 : 10′-*bis*-4-*carboxy*-5 : 10-*dihydrophenarsazine* (IV), and this compound is soluble in sodium hydroxide.





By a similar procedure, starting from *m*-aminobenzoic acid and *o*-bromophenylarsinic acid, 10-*chloro*-5 : 10-*dihydrophenarsazine*-3-*carboxylic acid* (V) was obtained which was even less soluble than the isomeric compound.

We have not succeeded in isolating the corresponding condensation products, using *p*-aminobenzoic acid and *N*-methylanthranilic acid.

EXPERIMENTAL.

2-*Carboxydiphenylamine*-6′-*arsinic Acid* (I).—A mixture of anthranilic acid (13·6 g.), *o*-bromophenylarsinic acid (14·0 g.), anhydrous potassium carbonate (14·0 g.), nitrobenzene (100 c.c.), and a trace of copper powder was boiled under reflux for 7 hours. After all volatile matter had been removed by distillation in steam, the resulting solution was boiled with charcoal, filtered, and acidified. The crude acid (11·0 g.) crystallised from acetic acid in colourless, silky needles, m. p. 243° (decomp.) (Found: As, 22·3. $C_{13}H_{12}O_5NAs$ requires As, 22·25%).

Reduction of 2-*Carboxydiphenylamine*-6′-*arsinic Acid.*—A solution of the acid (5 g.) in alcohol (20 c.c.) and concentrated hydrochloric acid (20 c.c.) containing a trace of iodine was heated to boiling, and sulphur dioxide passed into it for a few minutes. A yellow precipi-

tate formed immediately. The mixture was cooled rapidly, and the solid material separated. This substance was not homogeneous, since on recrystallisation from acetic acid it gave two types of crystals, yellow needles and transparent needles. This result indicated that reduction had taken place and that a partial elimination of hydrogen chloride had been effected.

10-*Chloro*-5 : 10-*dihydrophenarsazine*-4-*carboxylic acid* (III) was prepared by working up the crude reduction product in two ways : (*a*) A solution of the crude reduction product in the minimum quantity of hot acetic acid was boiled under reflux for 3 hours. On cooling, a homogeneous mass of yellow crystals separated. These were recrystallised from acetic acid and obtained in yellow needles, m. p. 243° (decomp.). (*b*) The crude material from the reduction of 5 g. of the original acid was dissolved in 3*N*-sodium hydroxide (75 c.c.), and the colourless solution boiled for a few minutes. On acidifying the cold solution with an excess of concentrated hydrochloric acid, the product separated as a yellow powder. This, after recrystallisation from acetic acid, was identical with the product previously obtained (Found : As, 23·4. $C_{13}H_9O_2NClAs$ requires As, 23·3%).

10 : 10′-*Bis*-4-*carboxy*-5 : 10-*dihydrophenarsazine* (IV).—A solution of 10-chloro-5 : 10-dihydrophenarsazine-4-carboxylic acid (2 g.) in acetic acid (20 c.c.) containing a trace of iodine was mixed with a solution of hypophosphorous acid (5 c.c.; *d* 1·136). Almost immediately an orange-coloured precipitate separated. This was filtered off, washed with acetone, and dried. The compound, m. p. 253° (decomp.), was practically insoluble in the usual organic solvents, but dissolved in sodium hydroxide, giving an orange-coloured solution (Found : As, 25·9. $C_{26}H_{18}O_4N_2As_2$ requires As, 26·2%).

3-*Carboxydiphenylamine*-6′-*arsinic acid*,

$$CO_2H{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_4{\cdot}AsO(OH)_2,$$

was prepared from *o*-bromophenylarsinic acid and *m*-aminobenzoic acid in a similar manner to the corresponding 2-carboxydiphenylamine-6′-arsinic acid, amyl alcohol being used instead of nitrobenzene for the condensation. It crystallised from dilute acetic acid in colourless needles, m. p. 238—239° (decomp.) (Found : As, 21·9. $C_{13}H_{12}O_5NAs$ requires As, 22·25%).

10-*Chloro*-5 : 10-*dihydrophenarsazine*-3-*carboxylic Acid* (V).—The reduction of 3-carboxydiphenylamine-6′-arsinic acid was carried out in a similar manner to that of the isomeride. The crude chloro-compound was dissolved in hot sodium hydroxide solution, and precipitated from the cold solution with an excess of concentrated hydrochloric acid. The yellow precipitate was very sparingly

soluble in all organic solvents and therefore difficult to obtain pure. It did not melt below 300° (Found: As, 22·8. $C_{13}H_9O_2NClAs$ requires As, 23·2%).

GUY'S HOSPITAL MEDICAL SCHOOL,
LONDON, S.E. 1.

[*Received, December 7th*, 1926.]

XL.—*The Nature of the Alternating Effect in Carbon Chains. Part X. The Nitration of Some Derivatives of β-Phenylethylamine.**

By FRANK ROBERT GOSS, WALTHER HANHART, and CHRISTOPHER KELK INGOLD.

To facilitate the development of the theory of reactivity-transmission by the Lewis electron-displacement mechanism, Goss, Ingold, and Wilson's quantitative study of the substitution of benzylamine derivatives (J., 1926, 2440) has now been supplemented by a similar study of the nitration of some derivatives of β-phenylethylamine. Here the electron-attracting centre is separated from the nucleus by an additional methylene group, and its *m*-directive effect should accordingly be weaker.

Experience having shown that the replacement of one alkyl group by another in a secondary, a tertiary, or a quaternary benzylamine has a relatively small influence on the degree of *m*-substitution observed in each class (*loc. cit.*), we have restricted the present investigation of β-phenylethylamine derivatives to an examination of the primary base, and one secondary, one tertiary, and one quaternary derivative. The results are in the following table, in which the data for the corresponding derivatives of benzylamine also are set forth for comparison.

Nitration of Derivatives of Benzylamine and β-Phenylethylamine in Nitric Acid (d 1·5) *at* −10° *to* 0°.

Benzylamine bases.		β-Phenylethylamine bases.	
Side chain.	Proportion of *m*-substitution.	Side chain.	Proportion of *m*-substitution.
$-CH_2\cdot NH_2$	49%	$-CH_2\cdot CH_2\cdot NH_2$	12%
$-CH_2\cdot NHMe$	69 ,,	$-CH_2\cdot CH_2\cdot NHMe$	15 ,,
$-CH_2\cdot NMe_2$	58 ,,	$-CH_2\cdot CH_2\cdot NMe_2$	13 ,,
$-CH_2\cdot NMe_3^+$	88 ,, †	$-CH_2\cdot CH_2\cdot NMe_3^+$	19 ,, †

† Picrate used.

* These experiments and a corresponding series on γ-phenylpropylamine derivatives were completed in all essentials at the date of the appearance of Ing and Robinson's statement (J., 1926, 1656) that they were investigating a compound of each class.

From these figures, it will be evident that the effect originating in the positively charged nitrogen atom suffers such loss by transmission through the additional carbon atom that the resulting *m*-substitution is diminished in ratios of approximately 1/4—1/5.

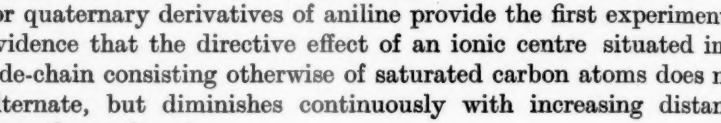
β-Phenylethylamine has been previously nitrated by Ehrlich and Pistschimuka (*Ber.*, 1912, **45**, 2428), who isolated the *p*-nitro-compound and one other product which they regarded as the *m*-derivative (yield 18%; m. p. of hydrochloride "gegen 160°"). We think, however, that this could not have been the pure *m*-compound, since our specimen of its hydrochloride melts 45° higher. On the other hand, the m. p. and properties of Ehrlich and Pistschimuka's product agree almost exactly with those of our *o*-compound. Further, the quantity of "meta-" derivative obtained by Ehrlich and Pistschimuka is 1½ times as great as the total amount (12%) estimated to be contained in our nitration products, and experience of the separation of the three isomerides has left us with the impression that it would be difficult to isolate in the pure condition more than a moderate fraction of the quantity of *m*-derivative actually present. On the other hand, the proportion of the *o*-compound formed on nitration under our conditions is considerably greater (25%), and therefore it might be possible to isolate as much as 18% of this substance. Methyl-β-phenylethylamine does not appear to have been nitrated previously. Dimethyl-β-phenylethylamine was nitrated by Barger (J., 1909, **95**, 2195), who obtained the *p*-compound; we have also separated some of the *m*-isomeride, and have isolated all three isomerides from the nitration product of trimethyl-β-phenylethylammonium picrate.

The figures in the last column of the table are based on the weights of unrecrystallised *m*-nitrobenzoic acid separated as previously described (Baker and Ingold, J., 1926, 2462) from the mixtures of nitrobenzoic acids formed by oxidation, either of the original mono-nitration products or of the residues remaining after partial separations of pure isomerides. The oxidation yields were mostly quantitative and the separation of the acids was again checked on artificial mixtures and was shown to give results correct to about 1·5%. Also by oxidation of the pure *o*-, *m*-, and *p*-isomerides it was shown that each gave the same (generally quantitative) yield of the corresponding nitrobenzoic acid; further, by oxidation of artificial mixtures of isomeric nitro-bases of similar composition to the nitration products, and subsequent separation of the acids, the proportions of the isomerides were satisfactorily estimated; it is therefore hoped that the figures submitted are not seriously in error.

Summarising these results, then, it appears that the work now

described provides the first clear proof of the formation of *m*-derivatives by direct nuclear substitution of β-phenylethylammonium compounds, and we can recall no other example of *m*-substitution in which the *m*-directing group is separated from the nucleus by two saturated carbon atoms. Further, the new results combined with those obtained by Vorländer and Siebert (*Ber.*, 1919, **52**, 294) for quaternary derivatives of aniline provide the first experimental evidence that the directive effect of an ionic centre situated in a side-chain consisting otherwise of saturated carbon atoms does not alternate, but diminishes continuously with increasing distance from the nucleus * :

Theoretical Order :



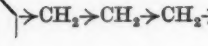
The lower values for the primary, secondary, and tertiary β-phenylethylamine salts, as compared with that obtained for the quaternary salt, are attributed to partial compensation by the negative end of the dipolar group (Goss, Ingold, and Wilson, *loc. cit.*; and following paper).

EXPERIMENTAL.

(A) *Nitration of β-Phenylethylamine.*

(i) *Qualitative Separation of Isomerides.*—The base (10 g.) was run in the course of 1·5 hours into nitric acid (50 c.c.; $d^{15°}$ 1·50) at −10°. Nitration appeared to follow almost instantaneously, but the mixture was warmed to 0° before being mixed with ice and basified with sodium hydroxide. The products then extracted with ether were isolated as their hydrochlorides by re-extracting the ethereal solution with sufficient dilute hydrochloric acid and evaporating this solution to dryness (Found: Cl, 17·4. $C_8H_{10}O_2N_2$,HCl requires Cl, 17·5%).

A single crystallisation from the minimal quantity of boiling 95% alcohol yielded 8·7 g. of almost colourless plates, m. p. 209—210°. This is the recorded m. p. of *p*-nitro-β-phenylethylammonium chloride. On oxidation by permanganate, *p*-nitrobenzoic acid was formed (yield 99%; m. p. 230—231°; mixed m. p. 232—233°). A further 1·0 g. of the same hydrochloride was obtained from the residue remaining on evaporation of the alcoholic mother-liquor by

* Mr. I. S. Wilson has obtained the approximate value 5 ± 2% for  by nitration of the picrate under similar conditions.

diluting its solution in the minimal quantity of boiling absolute alcohol with 800 c.c. of chloroform and allowing 24 hours for crystallisation; in another otherwise identical experiment the same result was achieved by extracting the residue with a warm alcohol–chloroform mixture (1 : 4), in which the *p*-compound remains undissolved. Total yield, 58%.

The *o*-derivative was next isolated by evaporating the chloroform and alcohol, and crystallising the residue from a small quantity of absolute alcohol at 0°. The crystals obtained were washed with alcohol–chloroform and the undissolved portion was crystallised 2—3 times from ethyl acetate containing the minimal quantity of alcohol necessary for solution (yields, up to 9%). o-*Nitro*-β-*phenylethylammonium chloride* crystallises as flattened needles or leaflets, m. p. 162—163° (Found: C, 47·1; H, 5·9. $C_8H_{11}O_2N_2Cl$ requires C, 47·4; H, 5·4%). On oxidation with potassium permanganate, it gives *o*-nitrobenzoic acid. (Yield of unpurified acid, 100%; m. p. 140—141°; mixed m. p. with genuine *o*-acid 141—144°, and with genuine *m*-acid 100—110°; after crystallisation from water, m. p. 141°; after crystallisation from chloroform, m. p. 144—145° and mixed m. p.'s with the *o*- and *m*-acids 144—145° and 105—110°, respectively. These particulars are recorded because Ehrlich and Pistschimuka, by oxidising their "meta" salt, obtained an acid which, after crystallisation from water, had m. p. 140°. This is the m. p. of pure *m*-nitrobenzoic acid, but it is also that of the *o*-nitrobenzoic acid obtained by us by oxidation and crystallised from water.)

The genuine *m*-derivative was isolated as its *oxalate* by basifying the residue from the combined mother-liquors with sodium hydroxide, extracting it with ether, precipitating the salt with anhydrous oxalic acid in dry ethereal solution, and crystallising it from 90% alcohol until the m. p. rose to and remained constant at 200° (decomp.) (Found: C, 46·7; H, 4·8. $C_{10}H_{12}O_6N_2$ requires C, 46·9; H, 4·7%). m-*Nitro*-β-*phenylethylammonium chloride*, which separates from alcohol in platelets or flattened needles, has m. p. 204—205° (Found: C, 47·5; H, 5·5; N, 13·6. $C_8H_{11}O_2N_2Cl$ requires C, 47·4; H, 5·4; N, 13·8%). On oxidation by permanganate, *m*-nitrobenzoic acid was obtained. (Yield, before purification, 102%; m. p. 131—135°; mixed m. p. with genuine *m*-acid 138—140°, and with *o*-acid 100—110°; after one crystallisation from ethyl acetate–ligroin, m. p. 139—140°, mixed m. p. with *m*-acid, 139—140°, and with *o*-acid 105—115°.)

(ii) *Estimation of Isomerides.*—Since the three isomerides can be oxidised practically quantitatively to the readily separable nitrobenzoic acids, it was decided to employ that method (Baker

and Ingold, *loc. cit.*) for the estimation of the proportions, although, preliminary experiments having shown that the *o*- and *p*-derivatives do not lose their side chains on reduction and subsequent bromination, it is probable that this method also would have worked (Goss, Ingold, and Wilson, *loc. cit.*).

(*a*) The base (10·00 g.) was nitrated as described above, and the main quantity of *p*-nitro-derivative removed as hydrochloride (7·68 g. = 46%). The residues (7·48 g. = 45%) were intimately ground and 2·00 g. were oxidised by gradually adding the theoretical quantity of 3% permanganate solution to a boiling solution of the salt in 200 g. of water, the addition being timed to keep pace with decolorisation. The yield of mixed acids was 1·60 g. (=97%) (Found: *M*, 167. Calc.: *M*, 167. Benzoic acid, by sublimation, 0·25%). The separation was performed with 1·512 g. after the removal of the benzoic acid. The *p*-acid (21%) * had m. p. 232°, mixed m. p. 233—235°; the *m*-acid (26%) * had m. p. 130°, mixed m. p. 136—138°, and, after one crystallisation from ligroin–ethyl acetate, m. p. 139—140°. Hence the original nitration product is estimated to have contained, *para* = (46 + 0·21 × 45)/91 = 61%; *meta* = 0·26 × 45/91 = 13%; *ortho* (by difference only) =26%.

An artificial mixture of the *p*-, *m*-, and *o*-hydrochlorides in the respective proportions 62·3%, 14·1%, 23·6%, on oxidation gave nitrobenzoic acids (yield 99%), which on separation yielded 61·7% of *p*-acid, m. p. 230—234°, mixed m. p. 234—235°, and 13·0% of *m*-acid, m. p. 132—133°, mixed m. p. 137—139°.

(*b*) The base (10·00 g.) was nitrated, and the diluted acid solution was extracted with ether, basified with alkali, and then again extracted. The second extract was dried with sodium sulphate, precipitated with dry hydrogen chloride, and then completely evaporated. The residue (16·3 g. = 97%) after grinding was oxidised (2·00 g.) as before (yield 1·61 g. = 98%; *M*, 168; benzoic acid, nil), and the isomeric acids were separated. The *p*-acid (65%) had m. p. 229—234°, mixed m. p. 232—235°; and the *m*-acid (11%) had m. p. 129—133°, mixed m. p. 138—140°.

(*c*) A portion (10·00 g.) of the mixed hydrochlorides obtained in experiment (*b*) was separated into 5·01 g. of *p*-nitro-β-phenylethylammonium chloride and 4·97 g. of residues (0·02 g. lost). The residues were oxidised as usual (yield 4·03 g. = 98·5%; *M*, 166, 166; benzoic acid 0·35%), and the acids separated. The *p*-acid (28%) had m. p. 234—235°, mixed m. p. 234—235°; the *m*-acid (26%) had m. p. 133—136°, mixed m. p. 139—140°. Hence the

* These and the other percentages of *p*- and *m*-nitrobenzoic acids given in this section are already corrected for the solubility of the *p*-acid and the *m*-barium salt (Baker and Ingold, *loc. cit.*).

original mixture is estimated to have contained, *para* = (50·1 + 49·7 × 0·28)/99·8 = 64%; *meta* = 49·7 × 0·26/99·8 = 13%; *ortho* (by difference) 23%.

(B) *Nitration of Methyl-β-phenylethylamine.*

(*d*) The base (4·5 g.) was nitrated at −10° to −5° with 30 g. of nitric acid (*d* 1·5), the conditions being otherwise as described for experiment (*a*); the product (yield 97·5%) was isolated as hydrochlorides, as in experiment (*b*), and oxidised in the usual way. The mixed nitrobenzoic acids (yield 101%; *M*, 167, 168; benzoic acid, nil) on separation contained *p*-nitrobenzoic acid (61%) having m. p. 233—234°, mixed m. p. 234—235°, and *m*-nitrobenzoic acid (15%), m. p. 125—135°, mixed m. p. 139—140°, m. p. after one crystallisation 140°.

(*e*) The picrate (m. p. 140—141°; Johnson and Guest, *Amer. Chem. J.*, 1909, **42**, 340) of the base was nitrated in 7·5 parts of nitric acid (*d* 1·50) at −10° to −5° and the product was mixed with ice, extracted with benzene, basified and extracted with ether. The residue from the ether on precipitation in benzene solution with picric acid gave 93·2% of mixed picrates. These were oxidised as usual (excepting that permanganate sufficient to destroy the picrate ions was added rapidly, and only the remaining quantity cautiously) and gave 97·6% of mixed acids (*M*, 166, 167. Benzoic acid, nil). The separated *p*-acid (65%) had m. p. 230—235°, mixed m. p. 233—235°, and the *m*-acid (15%) m. p. 125—135°, mixed m. p. 139—140°.

(C) *Nitration of Dimethyl-β-phenylethylamine.*

(i) *Qualitative Separation of Isomerides.*—The base was nitrated in the form of its picrate (7·5 g.) with nitric acid (45 g.; *d* 1·50) at −10°, and at the end of the process the temperature was allowed to rise to 0°; ice was then added, and, after extraction of the picric acid and any neutral by-products with benzene, the nitro-bases were liberated with sodium hydroxide and extracted with ether. In one experiment, the product (yield 90%) was isolated as picrates, and in another as oxalates, by precipitation in each case with the appropriate acid in dry benzene and ether respectively.

Dimethyl-*p*-nitrophenylethylammonium oxalate (Barger, J., 1909, **95**, 2195) may be obtained from the mixed oxalates, but owing to the sparing solubility of the *m*-oxalate, this method is less satisfactory than the separation of the *p*-nitro-picrate from the mixed picrates, by crystallisation from acetone–benzene (1 : 6) or acetone–alcohol. *Dimethyl-*p*-nitro-β-phenylethylammonium picrate* crystallises both in well-defined needles and in cubes, the

latter modification being apparently the more stable, m. p. 162° (Found: C, 45·1; H, 4·1. $C_{16}H_{17}O_9N_5$ requires C, 45·4; H, 4·0%). Oxidation with permanganate gave *p*-nitrobenzoic acid (yield 100%; m. p. 234—235°).

The same compounds were prepared from the primary salts as follows. *p*-Nitro-β-phenylethylammonium chloride (8 g.) and 38% aqueous formaldehyde (16 c.c.) were heated together at 135° for 3 hours, and the bases liberated by the addition of sodium hydroxide to the cooled solution extracted with ether. The oxalate, m. p. 154°, precipitated by the addition of dry ethereal oxalic acid was identical with the separated oxalate (above), and the similarly prepared picrate with the separated picrate.

Dimethyl-m-*nitro*-β-*phenylethylammonium oxalate* was isolated from the oxalate mixture by repeatedly crystallising it from 95% alcohol and diluting the filtrates of the later crystallisations with 100% alcohol; needles, m. p. 186°, then separated (Found: C, 50·5; H, 5·7. $C_{12}H_{16}O_6N_2$ requires C, 50·7; H, 5·7%). The *picrate*, prepared by precipitation of an alcoholic solution of the oxalate with picric acid, formed stout needles or prisms, m. p. 166—167° (Found: C, 45·4; H, 4·4. $C_{16}H_{17}O_9N_5$ requires C, 45·4; H, 4·0%). On oxidation of the oxalate with nitric acid, *m*-nitrobenzoic acid was obtained, and the same acid (m. p. 134—138°, mixed m. p. 139—140°) was obtained in 99% yield by the action of permanganate on the picrate.

We did not encounter the *o*-nitro-salts in the course of the above separations, but in order to study its behaviour on oxidation, we prepared *dimethyl*-o-*nitro*-β-*phenylethylammonium picrate* from the hydrochloride of the primary *o*-nitro-base by the formaldehyde method described above. The salt crystallised from alcohol–acetone in yellow prisms, m. p. 160—161° (Found: C, 45·8; H, 4·1. $C_{16}H_{17}O_9N_5$ requires C, 45·4; H, 4·0%). On oxidation with permanganate by the usual method, it gave *o*-nitrobenzoic acid. (Yield, unpurified, 102%; m. p. 138—142°, mixed m. p. 140—143°; crystallised from chloroform, m. p. 146°, mixed m. p. 146°.) Although the three isomeric picrates melt at not very different temperatures, they depress each other's m. p. by 15—30°.

(ii) *Estimation of Isomerides.*—(*f*) The nitration product isolated in the form of picrates (yield 93%; Found: C, 45·5; H, 4·3. Calc.: C, 45·4; H, 4·0%), on oxidation as usual, gave nitrobenzoic acids in 101% yield (*M*, 168; benzoic acid, nil). A sample of the mixture on separation was found to contain 70% of *p*-nitrobenzoic acid (m. p. 234—235°, mixed m. p. 234—235°) and 12% of *m*-nitrobenzoic acid (m. p. 120—130°, mixed m. p. 133—136°; crystallised once, m. p. 139—140°, mixed m. p. 140°).

(*g*) By crystallisation from acetone–benzene the mixed picrates were divided into two portions constituting 66% and 34% of the whole. The first, on oxidation, gave acids (yield 100%; benzoic acid, nil) which, on separation, contained *p*-nitrobenzoic acid (yield 85%) having m. p. 232—233°, and mixed m. p. 233—238°, and *m*-nitrobenzoic acid (yield 11%) having m. p. 128—133°, mixed m. p. 136—138°. The second gave acids (yield 101%; benzoic acid 1·2%; *M*, 165, 166) which contained the *p*-acid (30%), m. p. 220—232°, mixed m. p. 225—235°, and the *m*-acid (19%), m. p. 130—137°, mixed m. p. 139—140°. The original mixture is therefore estimated to have contained *para* 66%, *meta* 14%, *ortho* (by difference) 20%.

(D) *Nitration of Trimethyl-β-phenylethylammonium Picrate.*

(i) *Qualitative Separation of Isomerides.*—Trimethyl-β-phenylethylammonium picrate (Decker and Becker, *Ber.*, 1912, **45**, 2404) was nitrated in nitric acid at −1—0°, and the nitric acid solution was warmed to 15°, mixed with ice (picric acid separated), just basified with concentrated sodium hydroxide solution, and cooled to −10°; the nitro-picrates then separated (α; yield 92%). The filtrate, on saturation with sodium picrate, yielded a further small quantity of crystalline material (β), and more was obtained from the mother-liquor by concentration and extraction with ethyl acetate (γ). The aqueous solution was finally evaporated to dryness, and the residue extracted with alcohol (δ).

The mixture (α), on crystallising twice from boiling alcohol, yielded pure *trimethyl*-p-*nitro*-β-*phenylethylammonium picrate* as yellow leaflets, m. p. 144—145° (yield 50%) (Found: C, 46·4; H, 4·5. $C_{17}H_{19}O_9N_5$ requires C, 46·7; H, 4·4%). The corresponding *iodide* forms pale yellow needles, m. p. 206° (Found: I, 37·5. $C_{11}H_{17}O_2N_2I$ requires I, 37·8%). This was prepared by boiling a benzene solution of dimethyl-*p*-nitrophenylethylamine (from 1·5 g. of oxalate) with sodium carbonate (2 g.) and methyl iodide (2·3 c.c.) for 3 hours, washing the salts with hot benzene, and extracting the quaternary iodide with hot alcohol, from which it separated on cooling. The above picrate was also prepared from *p*-nitrophenylethylammonium chloride (0·75 g.) by boiling its solution in absolute alcohol (20 c.c.) for 2 hours with methyl sulphate (2·5 c.c.) and sodium carbonate (2 g.). After water had been added, and the alcohol boiled off, the solution was extracted with ether, and the quaternary picrate precipitated by addition of a solution of sodium picrate to the aqueous solution (yield 55%). On oxidation by permanganate *p*-nitrobenzoic acid was formed (yield 100%; m. p. 230—235°; mixed m. p. 232—235°).

The mixtures (β), (γ), and (δ) contained sodium salts, from the bulk of which they were freed by washing with cold water. The products thus partly purified were crystallised *slowly* from boiling alcohol or water, and the three isomerides separated by mechanical means. The *p*-picrate was the only one which separated in plates; the other two formed needles, but those of the *o*-compound were of a paler yellow colour than those of the *m*-isomeride.

Trimethyl-m-*nitro*-β-*phenylethylammonium picrate* separates from alcohol in short needles (especially when slightly impure), and when pure, in felted masses of flexible, hair-like crystals, m. p. 147—148° (Found: C, 46·7; H, 4·5. $C_{17}H_{19}O_9N_5$ requires C, 46·7; H, 4·4%). Mixtures with the *o*- and *p*-isomerides melted at about 125°. The same substance was prepared from *m*-nitro-β-phenylethylammonium chloride by methylation with methyl sulphate as described above. On oxidation by permanganate *m*-nitrobenzoic acid was obtained in 100% yield (m. p. 135—136°; mixed m. p. 139—140°).

The *trimethyl*-o-*nitro*-β-*phenylethylammonium picrate* obtained as described above was identical with the picrate obtained from the product of the action of the alcoholic methyl sulphate and sodium carbonate on *o*-nitro-β-phenylethylammonium chloride, and with the picrate which was precipitated when *o*-nitro-β-phenylethyldimethylamine was mixed with *s*-trinitroanisole in benzene solution. Crystallised from alcohol, it formed bright yellow, brittle needles, m. p. 146—147° (Found: C, 46·7; H, 4·5. $C_{17}H_{19}O_9N_5$ requires C, 46·7; H, 4·4%). The yield of *o*-nitrobenzoic acid (m. p. 145—147°; mixed m. p. 145—147°; mixed m. p. with *m*-nitrobenzoic acid 110—120°) obtained on oxidation by permanganate was 100%.

(ii) *Estimation of Isomerides.*—(*h*) The quaternary picrate (8·00 g.) was added to 60 g. of nitric acid ($d^{16°}$ 1·50) at −5° during 10 minutes, and the product was warmed to 10° during 5 minutes, kept at 10° for 15 minutes, and then mixed with ice and worked up for the *p*-compound as described above. The pure *p*-compound isolated weighed 4·75 g., and the combined residues, when freed from sodium salts, etc., 3·94 g. The total yield was therefore 97·5%, the *p*-isomeride constituting 55% and the residues 45% of this isolated material. On oxidation by the customary method, nitrobenzoic acids (*M*, 166, 165, 166; benzoic acid, nil) were obtained in 89% yield, and this mixture contained 33% of *p*-nitrobenzoic acid (m. p. 230—235°) and 38% of *m*-nitrobenzoic acid (m. p. 120—135°, mixed m. p. 137—140°; after one crystallisation from ethyl acetate, m. p. 138—140°, mixed m. p. 139—140°). The original nitration product

is therefore estimated to have contained: *para*, $55 + 0{\cdot}33 \times 45 = 70\%$; *meta*, $0{\cdot}38 \times 45 = 17\%$; *ortho* (by difference), 13%.

An artificial mixture of *p*-, *m*-, and *o*-picrates in the respective proportions, 68·4%, 19·9%, 11·7%, on oxidation gave a 97% yield of nitrobenzoic acids, which on separation gave 67·0% of *p*-acid, m. p. 233—234°, mixed m. p. 235°, and 19·1% of *m*-acid, m. p. 128—133°, mixed m. p. 136—139°.

(*i*) Another oxidation of the same mixture yielded 91% of mixed nitrobenzoic acids (*M*, 167, 168; benzoic acid, nil), and the mixture, on separation, was found to contain 24% of *p*-acid (m. p. 200—230°; mixed m. p. 225—235°) and 46% of *m*-acid (m. p. 115—130°; mixed m. p. 133—138°; m. p. after one crystallisation from ethyl acetate–ligroin, 137—140°). For the original nitration product this gives: *para*, 66%; *meta*, 21%; *ortho* (by difference) 13%. In view of the fact that in this and the previous experiment the mixed nitrobenzoic acids were obtained in only 90± 1% yield, these figures are regarded as rather less accurate than the others given in this paper.

(E) *Nitration of Trimethylbenzylammonium Picrate.*

For the sake of the numerical comparison on p. 250 this substance was prepared and nitrated under the conditions employed in example (D) and in the case of triethylbenzylammonium picrate (Goss, Ingold, and Wilson, *loc. cit.*), and the proportions of the isomerides were estimated. Ing and Robinson (*loc. cit.*) nitrated trimethylbenzylammonium nitrate and isolated 73·6% of pure *m*-derivative.

Benzyldimethylamine and trinitroanisole (1 mol.) were heated together in benzene solution at 70—75° for 0·5 hour, and the *trimethylbenzylammonium picrate* was collected and crystallised from alcohol, from which it separated in clusters of yellow prisms, m. p. 168—169° (Found: C, 51·2; H, 5·1. $C_{16}H_{18}O_7N_4$ requires C, 50·8; H, 4·8%).

The bulk of the nitration product was precipitated with gaseous ammonia (*loc. cit.*), the neutral filtrate evaporated to dryness, and the residue, after grinding with a little cold water, crystallised from boiling water. Total yield 93·6% (Found: C, 45·6; H, 3·7. $C_{16}H_{17}O_9N_5$ requires C, 45·4; H, 4·0%).

Separation.—The principle employed was that crystallisation from or extraction with concentrated alcohol favours the isolation of the *m*-compound, whilst in dilute alcohol or water this isomeride is relatively easily soluble. The well-ground and mixed nitration product (10·00 g.) was boiled with a large bulk of absolute alcohol, the solution filtered while still hot, and the residue crystallised from

50% alcohol (7·30 g. of meta, m. p. 179·5—180·5°). The aqueous-alcoholic solution was concentrated and alcohol was added (0·67 g. of meta, m. p. 179—180°), and the combined aqueous and alcoholic solutions were then evaporated to dryness and the residue was extracted with successive portions of hot absolute alcohol until the m. p. of the undissolved portion rose above 175°. This portion was then crystallised from 50% alcohol (0·42 g. of meta, m. p. 179—180°) and the filtrate was concentrated and mixed with alcohol as before (0·17 g. of meta, m. p. 178—179·5°). All liquors were now combined and evaporated and the residue was crystallised from water (0·23 g. of para, m. p. 193—194°), the filtrate being concentrated (0·12 g. of para, m. p. 192—194°) and mixed with alcohol (0·02 g. of meta, m. p. 178—179°). The totals separated are therefore : para 3·5%, meta 85·8% (total 89·3%). The mother-liquors were now distilled completely from a water-bath under slightly diminished pressure and the distillate was treated with sodium picrate prepared from 0·5 g. of picric acid, and with 0·67 g. of *m*-nitrobenzyltrimethylammonium picrate. The undissolved portion weighed 0·44 g., so that the saturated solution contained 0·23 g., and 0·62 g. of picrate ions. The quantity of picrate ions contained in the solution before the distillation was 0·59 g.

The residue from the distillation, on oxidation with 240 c.c. of 3% permanganate and 200 c.c. of water, gave 0·305 g. of acids, from which 0·201 g. of *p*-nitrobenzoic acid (m. p. 230—233°; mixed m. p. 232—234°) was obtained by digestion with chloroform (solubility correction, 0·026 g.), but the separation of *m*-nitrobenzoic acid through the barium salt was spoilt by the presence of oxalic acid. *p*-Nitrobenzyltrimethylammonium picrate (1·50 g.), on oxidation under the same conditions, gave 0·55 g. of *p*-nitrobenzoic acid (m. p. 234—235°)—that is, 90% of the theoretical—so that the *p*-nitrobenzoic acid isolated by oxidation of the residues may be taken to correspond with 0·64 g. of the *p*-picrate.

Hence, for the original nitration product, we have :

	Separation.	Solubility.	Oxidation.	Total.
Ortho-	—	—	—	—*
Meta-	85·8	2·3	—	88%
Para-	3·5	—	6·4	10 „

* The figure, 2%, obtained by difference is without significance.

For use in identifying the separated products, the *m*- and *p*-nitro-compounds were prepared from the appropriate tertiary base and trinitroanisole. m-*Nitrobenzyltrimethylammonium picrate* separates from water in pyramid-capped prisms or stout rhombs, m. p. 180—180·5° (Found : C, 45·7; H, 4·2. $C_{16}H_{17}O_9N_5$ requires

C, 45·4; H, 4·0%). It is very sparingly soluble in boiling methyl or ethyl alcohol. p-*Nitrobenzyltrimethylammonium picrate* separates from water or ethyl alcohol in fern-like aggregates of leaflets or flattened needles, m. p. 194° (Found: C, 45·8; H, 4·1%).

THE UNIVERSITY, LEEDS. [*Received, September 29th*, 1926.]

XLI.—*The Nature of the Alternating Effect in Carbon Chains. Part XI. Further Evidence on the Substitution of Benzylamine Salts.*

By JOHN WILLIAM BAKER and CHRISTOPHER KELK INGOLD.

IT has previously been suggested (Goss, Ingold, and Wilson, J., 1926, 2440) that the formation of comparatively large quantities of *m*-isomeride in the nitration of benzylamine salts arises from the action of the dipole contained in the salt grouping, which sets up electronic strain of a similar kind to that produced by the free charge in the corresponding ion (I; A = H); and in support of this view it has, *inter alia*, been shown (Baker and Ingold, J., 1926, 2462) that phenylnitromethane, a substance analogous to a benzylamine salt but containing a stable dipole (I; A = O), nitrates in the *m*-position to approximately the same extent as benzylamine itself.

(I.) $C_6H_5 \rightleftarrows CH_2 \rightleftarrows \overset{+}{N}—\overset{-}{A}$ { → electron attraction towards +; ← partly compensating repulsion from −.

Although this result was predicted from the analogous constitution of the two types, agreement in a single case may possibly be fortuitous, and it was therefore considered desirable to extend the comparison to a series of substituted benzylamines (II) and the corresponding phenylnitromethane derivatives (III) in order to ascertain if the agreement were general.

(II.) $C_6H_5 \cdot CRR' \cdot \overset{+}{N}H_2—\overset{-}{H}X$ $\qquad$ $C_6H_5 \cdot CRR' \cdot \overset{+}{N}(=O)—\overset{-}{O}$ (III.)

The nitration of benzylamine itself (II; RR′ = H_2), of β-nitro-β-phenylpropane (III; RR′ = Me_2), and of phenylnitromethane (III; RR′ = H_2) had already been carried out, and in this paper the nitration of α-phenylethylamine (II; RR′ = MeH), α-phenyl-*iso*propylamine (II; RR′ = Me_2), and α-nitro-α-phenylethane (III; RR′ = MeH) is described. The results obtained render possible a comparison between the three pairs of analogously constituted benzylamine and phenylnitromethane derivatives.

The proportion of *m*-isomeride formed in each case is indicated in the following table:

Type.	RR′ = H_2.	RR′ = MeH.	RR′ = Me_2.
$C_6H_5 \cdot CRR' \cdot NH_2X$	49	40	26 % meta-derivative.*
$C_6H_5 \cdot CRR' \cdot NO_2$	50	43	27 „ „ „ *

* Estimated from the weights of separated but unrecrystallised *m*-nitrobenzoic acid obtained after oxidation of the mixed isomerides (compare preceding paper).

In all three cases the anticipated agreement is found to exist.

Experimental.

In this section, only those details are recorded which could not be inferred from the experimental descriptions given in Parts VIII, IX, and X (J., 1926, 2440, 2462; preceding paper).

(i) *Nitration of α-Nitro-α-phenylethane.*—The nitro-compound (b. p. 126—130°/30 mm.), prepared as already described (Baker and Ingold, *loc. cit.*), was nitrated at −15° with nitric acid ($d^{16°}$ 1·49). The rate of addition of the nitro-derivative to the acid was 1·0 g. per hour, and the mixture was kept for a further 3·0 hours at −15—−10° before being warmed to 0°; ice was then added. On being worked up as in the nitration of phenylnitromethane (*loc. cit.*), the nitration product (Found: C, 48·8; H, 4·6. Calc.: C, 48·6; H, 4·2%) was obtained; it crystallised almost completely, and a portion when drained had m. p. 80°. The total yield was 91%, and a further 3% of the material was accounted for as acid by-products. The whole nitration product, on oxidation by permanganate, gave mixed nitrobenzoic acids (Found: C, 50·4; H, 3·6. Calc.: C, 50·3; H, 3·0%) in 96% yield. The separated *p*-nitrobenzoic acid (34%) had m. p. 228° (mixed m. p. 231°). The separated *m*-nitrobenzoic acid (43%) was collected in two portions, one, the major portion (precipitated), having m. p. 136° (mixed m. p. 141°), and the second (extracted with ether) having m. p. 123° (mixed m. p. 134—135°).

(ii) *Nitration of α-Phenylethylamine.*—α-Phenylethylamine (10 g.) was nitrated with nitric acid (60 g.; $d^{16°}$ 1·50) at −10°. The addition occupied 3·5 hours, and the product was kept at −10° for a further 1·5 hours, warmed to 0° during 1·5 hours, and mixed with ice. After the extraction of neutral and acid by-products with ether, the nitro-bases were liberated by addition of sodium hydroxide and extracted with ether, and then re-extracted from the ethereal solution with dilute hydrochloric acid. The yield of hydrochlorides was 89% (Found: Cl, 17·7. Calc.: Cl, 17·5%). Oxidation by permanganate gave nitrobenzoic acids in a yield of 89% (Found: *M*, 167; benzoic acid, by sublimation, nil).

The separated *p*-nitrobenzoic acid (56%) had m. p. 229° (mixed m. p. 233—234°), and the *m*-acid (38%) m. p. 133° (mixed m. p. 139°).

The mixed hydrochlorides were converted into picrates and these were crystallised from 50% methyl alcohol. The crystallised portion (64%, m. p. 190—205°), on oxidation with permanganate, gave nitrobenzoic acids (Found : *M*, 168; benzoic acid, nil) in 85% yield. On separation, the *p*-acid (75%) had m. p. 234—235° (mixed m. p. 234—235°) and the *m*-acid (20%) had m. p. 131—137° (mixed m. p. 138—140°). The mother-liquor from the crystallisation of the picrates was evaporated with water to remove the methyl alcohol and oxidised; nitrobenzoic acids were then isolated in 82% yield (Found : *M*, 166; benzoic acid, 1·1%). The separated *p*-acid (17%) had m. p. 230—234° (mixed m. p. 232—235°), and the *m*-acid (78%) m. p. 129—136° (mixed m. p. 137—140°). After one crystallisation from ethyl acetate–ligroin, the latter melted at 140°. Combining the results obtained with these two picrate fractions, the original nitration product is estimated to have contained : para, $0{\cdot}17 \times 36 + 0{\cdot}75 \times 64 = 54\%$; meta, $0{\cdot}78 \times 36 + 0{\cdot}20 \times 64 = 41\%$. The mean of the two determinations gives *para* 55%, *meta* 40%.

(iii) *Nitration of α-Phenylisopropylamine.*—This base was prepared according to the scheme $CH_2Ph{\cdot}CN \longrightarrow CMeHPh{\cdot}CN \longrightarrow CMe_2Ph{\cdot}CN \longrightarrow CMe_2Ph{\cdot}CO{\cdot}NH_2 \longrightarrow CMe_2Ph{\cdot}NH_2$, Haller and Bauer's procedure (*Ann. Chim. Phys.*, 1918, **9**, 8) being followed in the first three stages. The last stage has been effected by Brander (*Rec. trav. chim.*, 1918, **37**, 67), who, however, records no detailed directions. Bromine (27 g.) and the amide (27 g.) were successively added to a solution of potassium hydroxide (9·5 g.) in water (90 c.c.), and the yellow suspension thus formed was gradually added with cooling to a solution of potassium hydroxide (28·5 g.) in water (300 c.c.). After heating on the water-bath for 1 hour, the mixture was cooled and extracted with ether, and the base was extracted from the ether with aqueous hydrochloric acid, liberated by the addition of alkali, and then re-extracted with ether. It had b. p. 94—95°/22 mm., and the hydrochloride had m. p. 240° (decomp.) (Found : Cl, 20·7. Calc. : Cl, 20·7%). The same base was also obtained in small yield by reduction of β-nitro-β-phenylpropane, as described by Konovalov (*J. Russ. Phys. Chem. Soc.*, 1894, **26**, 68); the hydrochloride obtained in this way had the same m. p., and a mixture with the other specimen showed no m. p. depression (Konovalov records m. p. 235·5°).

Nitration was effected at −10° with nitric acid ($d^{16°}$ 1·49), the speed of addition being 1·1 g. per hour. The product was kept

for a further 3 hours at about −10° and for 0·3 hour at 0°; ice was then added and the mixed nitro-bases were isolated as hydrochlorides. The yield was 95% (Found: Cl, 16·4. Calc.: Cl, 16·4%), and a further 2% of the material used was obtained as acid by-product, evidently formed by oxidation. The mixed chlorides, on oxidation with nitric acid, gave nitrobenzoic acids in 82% yield (Found: *M*, 165·5; benzoic acid, nil). The separated *p*-acid (58%) had m. p. 233—235° and the mixed m. p. was 234—235°. The *m*-acid was collected in two portions; one (precipitated; yield 19%) had m. p. 138—139°, the mixed m. p. being 140°, whilst the other (extracted; 8%) had m. p. 129—134° (mixed m. p. 137—139°), and on crystallisation from ethyl acetate–ligroin had m. p. 139—140°. The total *m*-acid was therefore 27%.

The mixed hydrochlorides (2·00 g.) were converted into picrates, which crystallised from 300 c.c. of boiling water in bunches of sulphur-yellow needles, m. p. 230° (1·68 g.). These, on crystallisation from 125 c.c. of boiling water, yielded 1·51 g. (40%) of crystals, m. p. 234°, and further crystallisation did not alter this m. p. This compound appears to be α-p-*nitrophenylisopropylammonium picrate* (Found: C, 44·5; H, 3·7. $C_{15}H_{15}O_9N_5$ requires C, 44·0; H, 3·7%), since oxidation of the corresponding nitrate with nitric acid gave *p*-nitrobenzoic acid, m. p. 230—233°, mixed m. p. 232—235°, in 86% yield. The combined mother-liquors, containing 60% of the original mixed picrates, were worked up for nitro-bases and these were oxidised; an 81% yield of nitrobenzoic acids was then obtained (Found: *M*, 168; benzoic acid, nil). The separated *p*-nitrobenzoic acid (33%) had m. p. 225—232°, mixed m. p. 229—234°; the *m*-acid was isolated in two portions, one (precipitated) having m. p. 136—139°, mixed m. p. 139—140° (32%), and the other (extracted from solution with ether) having m. p. 126—132°, mixed m. p. 136—140° (10%). The latter portion, after a single crystallisation from ethyl acetate–ligroin, had m. p. 140°. The original mixture of picrates is therefore estimated to have contained: para, $40 + 0{\cdot}33 \times 60 = 60\%$; meta, $0{\cdot}42 \times 60 = 25\%$. The mean of the two determinations gives *para*, 59%; *meta*, 26%.

We desire to thank the Royal Society for defraying part of the expense of this research.

THE UNIVERSITY, LEEDS. [*Received, September 29th*, 1926.]

XLII.—*The "Uniform Movement" of Flame in Mixtures of Hydrogen and Air.*

By ELIZABETH HELEN MACLEOD GEORGESON and FRANCIS JOHN HARTWELL.

THE measurement of the speed of the so-called "uniform movement" * of flame in gaseous mixtures has been found to be of considerable value as affording an indication of the relative rates of inflammation of different mixtures. The earlier methods of measuring this speed, which is not great in the majority of mixtures of inflammable gases with air, have usually depended upon the electrical registration of the time of fusion of fine screen-wires stretched at measured intervals across the tube in which the flame travels. This "screen-wire" method of measurement, although sufficiently accurate in experienced hands, is clearly not to be compared as regards general usefulness with the photographic method of analysing the movement of flames, using a rapidly revolving drum, which Professor H. B. Dixon has developed; for the latter method enables any slight variations in the speed of the flame from point to point along the tube to be detected, and ensures that if, as in the present instance, the speed of the uniform movement alone is required, no other phase in the propagation of flame (such as the "vibratory movement" which immediately succeeds the uniform movement) shall be included in the measurements, a matter which is sometimes by no means easy to arrange when the screen-wire method is used.

In connexion with other researches that are being carried out in these laboratories, it became necessary to obtain strictly comparable measurements of the speed of uniform movement of flame in mixtures of different inflammable gases (including hydrogen) with air, and it was decided to use the photographic method throughout. Photographic registration of the feebly actinic flames during the uniform movement in hydrogen–air mixture has presented considerable difficulty, but we have recently succeeded in obtaining satisfactory records, over a fairly wide range of mixtures, by using a tube of transparent quartz and photographing the flames through a quartz lens on Lumière bromide paper of special sensitivity. The outside of the tube was partly covered with black paper, leaving a horizontal slit 7 mm. wide throughout its length.

The quartz tube, which was 90 cm. long and of 2·4 cm. internal

* The uniform movement occurs when the inflammable mixture is contained in a horizontal tube, closed at one end and open at the other, and is ignited at the open end. It is usually maintained over about one-third of the length of the tube.

diameter, was supported horizontally and, as a precaution in the event of the detonation-wave being set up, was attached to a straight extension piece of lead piping, closed at the far end. The open end of the tube was provided with a flange, and a flanged cover, fitted with a tubulure and tap for the introduction of the explosive mixture, could be clipped thereto (see J., 1914, **105**, 2609). This cover was removed by gently sliding it upwards just before igniting the mixture, which was effected by passing a large flame comparatively slowly across the now open end of the tube. In this way, mechanical disturbance of the mixture at the moment of ignition was avoided and the mixture was ignited exactly at the open end. Unless these precautions were taken, and the same procedure adhered to rigidly, it was found that the " uniform movement " was not maintained over an appreciable distance of travel of the flame, or varied in speed from one experiment to another with a mixture of the same composition. Although precautions of the character described are required with all inflammable mixtures if accurate results are to be obtained, the uniform movement in mixtures of hydrogen and air seems to be particularly sensitive to extraneous disturbances.

Photographs were successfully obtained of the flames moving in mixtures containing between 20 and 50% of hydrogen. On either side of this range the records were too faint to measure. With each mixture three photographs were taken of successive lengths of 26 cm. of the tube, whence a composite photograph, showing the flame as it travelled from the open end over a distance of 79·5 cm. towards the closed end, was obtained. Typical photographs, reduced in size for reproduction, are shown on Plate I.

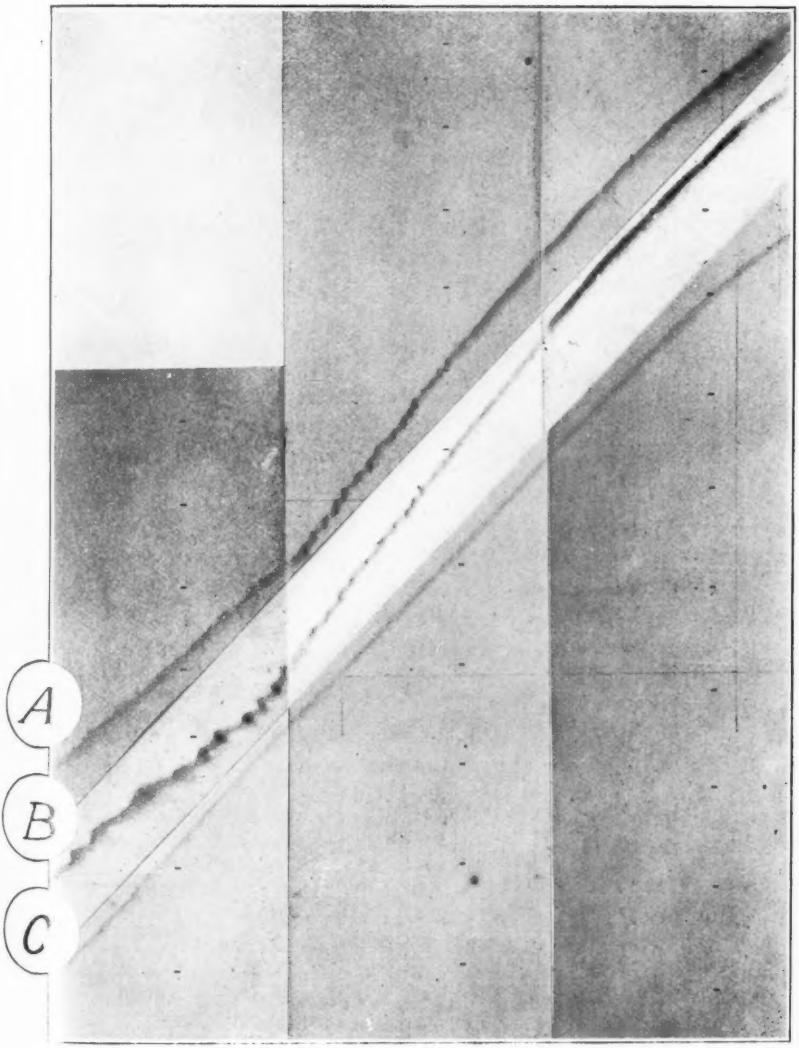
On close analysis of the movement of the flame, it was found that, in each mixture, its speed fluctuated during the first 26 cm. of travel, remained reasonably uniform over the next 26 cm.,* and then decreased slightly, antecedent to the vibratory movement, within the next 26 cm. We have therefore recorded, as the speed of " uniform movement " in the mixture concerned, that obtaining over the distance 29—55 cm. measured from the open end of the tube. Typical photographs of flames travelling in different mixtures over this section of the tube are reproduced in Plate II. The general results are recorded in Table I.

Apart from the anomalous results obtained with the 23·9 and 24·95% mixtures, which we are unable completely to explain,†

* Faint undulations that made their appearance during this period did not affect the mean speed of the flame.

† The vibratory movement apparently started earlier with these mixtures than with the others.

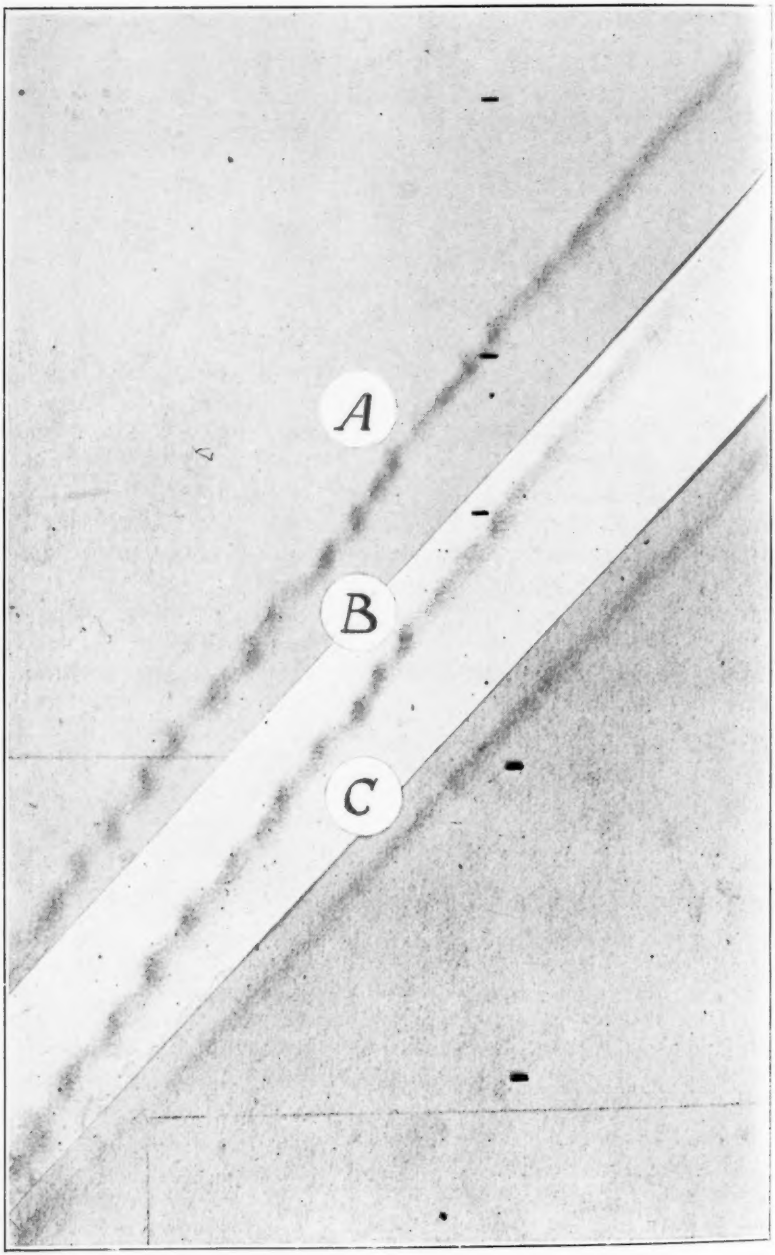
PLATE I.



The propagation of flame in mixtures of hydrogen and air.
A. 26·95%. B. 30·95%. C. 41·70%.

[*To face p.* 266.]

PLATE II.



The uniform movement of flame in mixtures of hydrogen and air.
A. 26·95%. B. 30·95%. C. 41·70%.

TABLE I.

The Uniform Movement of Flame in Mixtures of Hydrogen and Air.
(Tube 2·4 cm. in diameter.)

Comp. of mixture (hydrogen %).	Speed of uniform movement (cm. per sec.).	Comp. of mixture (hydrogen %).	Speed of uniform movement (cm. per sec.).
20·30	320, 323	36·70	474, 464
23·90	437, 414	37·50	520
24·95	462	40·45	478, 472
26·95	371, 362	41·70	501, 493
30·95	424, 418	45·45	433, 434
33·30	462, 461, 436	49·65	395, 393
34·90	501, 491		

these figures are comparable with those recorded by Haward and Otagawa (J., 1916, **109**, 83), when using a glass tube of 2·5 cm. internal diameter and measuring the mean speeds of the flames over the distance 10—50 cm., from the open end, by the screen-wire method.

A future communication will deal with the speed of the uniform movement in hydrogen mixtures in which the nitrogen of the air has been replaced by either argon or helium. A striking feature of the results is the high actinic value of the flames.

This work has been carried out for the Safety in Mines Research Board, to whom our thanks are due for permission to publish this paper.

SAFETY IN MINES RESEARCH LABORATORIES,
SHEFFIELD. [*Received, October 15th,* 1926.]

XLIII.—*The Normal Oxidation–Reduction Potential of Mercury.*

By SYDNEY RAYMOND CARTER and ROBERT ROBINSON.

THE normal oxidation potential of mercury has hitherto only been obtained by indirect methods, since most of the mercuric or mercurous salts suffer from one or more of the disadvantages of low solubility, small degree of ionisation, and a tendency towards the formation of complex salts and ions.

An examination of the mercurous and mercuric perchlorates shows that these salts are practically free from the above objections, and as they can be prepared in a state of purity they are suitable for a direct determination of this potential,

Preparation of Perchlorates.

Mercuric perchlorate was prepared according to Chikashigé (J., 1895, **67**, 1013) : a slight excess of red mercuric oxide was ground up with 2*N*-perchloric acid and, after filtration through asbestos, the solution was concentrated at 40—50° under reduced pressure until crystals separated. Evaporation under reduced pressure appeared to inhibit the formation of basic perchlorates. The crystals were recrystallised from water by a similar evaporation and then dissolved in water, giving a solution in which $[Hg(ClO_4)_2] = 0{\cdot}0922N$, the mercury being determined by precipitation with hydrogen sulphide. In preparing the solution of mercuric perchlorate for the second series of determinations, the salt was not isolated, the heated and filtered solution being diluted suitably.

Mercurous perchlorate was prepared (Linhart, *J. Amer. Chem. Soc.*, 1916, **38**, 2358) by treating perchloric acid with a slight excess of mercurous oxide, in contact with mercury. After standing for some time, the solution was filtered and allowed to remain in contact with mercury for several days. By precipitation with potassium chloride, it was found that $[Hg_2(ClO_4)_2] = 0{\cdot}080N$. The solution also contained a small amount of mercuric perchlorate equal to $0{\cdot}0148N$. In preparing the solution of mercurous perchlorate for the second series of experiments, mercuric perchlorate was reduced with mercury; reduction was not complete, the resulting solution containing a mixture of mercurous and mercuric perchlorates.

To check the purity of the solution of mercurous perchlorate, it was diluted to a strength of $0{\cdot}1N$-$\frac{1}{2}Hg_2(ClO_4)_2$, and the following cell constructed :

$$Hg|0{\cdot}1N\text{-}\tfrac{1}{2}Hg_2(ClO_4)_2|0{\cdot}1N\text{-}KNO_3|N\text{-}KCl|N\text{-}KCl,Hg_2Cl_2|Hg.$$

It was found to have a potential of 0·4720 and 0·4718 volt on two successive days. For a similar cell, Ley and Heimbucher (*Z. Elektrochem.*, 1904, **10**, 301) found the potential 0·4719 volt.

Construction of Cells.

The oxidation element consisted of about 100 c.c. of a solution prepared by mixing the above two solutions in the requisite proportions. Three electrodes of bright, unplatinised platinum foil were used, about 1 sq. cm. in area. The complete cell was :

$$Pt|Hg(ClO_4)_2,\ \underset{a}{Hg_2(ClO_4)_2|0{\cdot}1N\text{-}KNO_3}|\underset{b}{N\text{-}KCl}|N\text{-}KCl,Hg_2Cl_2|Hg.$$

The connecting syphon tubes at *a* and *b* were filled with the solution of the oxidation element and with *N*-KCl, respectively. The three electrodes gave perfect agreement between themselves, and the

potential was constant over several days. The cells could be reproduced with a variation of about 0·3 millivolt. After measuring the potential, the cell solution was analysed, mercurous mercury being estimated as calomel, whilst the mercuric mercury in the filtrate was determined as sulphide. All measurements were made at 18°; potentials were referred to the absolute scale and were given a positive sign if the current flowed through the cell from the normal calomel electrode.

The diffusion potentials at a and b have been shown by Ley and Heimbucher (*loc. cit.*) to be of a small order (less than 1 milllivolt), and have been neglected in this investigation.

Deduction of the Normal Oxidation Potential.

The behaviour of the system is determined by the equation:

$$E = E_0 + 0{\cdot}029 \log [Hg^{\cdot\cdot}]^2/[Hg_2^{\cdot\cdot}] \quad . \quad . \quad . \quad . \quad (1)$$

E_0 being the normal oxidation potential and E the potential of the half-element corresponding to the given mercurous- and mercuric-ion concentrations. Now if α_1 and α_2 are the degrees of dissociation of the mercuric and mercurous perchlorates, respectively, then

$$E = E_0 + 0{\cdot}029 \log \alpha_1^2[Hg(ClO_4)_2]^2/\alpha_2[Hg_2(ClO_4)_2] \quad . \quad . \quad (2)$$

which may be written:

$$E = E_0 + 0{\cdot}029 \log [Hg(ClO_4)_2]^2/[Hg_2(ClO_4)_2] + 0{\cdot}029 \log \alpha_1^2/\alpha_2 \quad (3).$$

The last term introduces a small correction, due to the incomplete dissociation of the perchlorates. Hence, if the potential of the half-element is known, and also the concentrations of the mercurous and mercuric perchlorates, then, by substitution in equation (3), E_0, the normal oxidation potential, may be calculated.

Correction for Incomplete Dissociation of the Perchlorates.—In order to obtain α_1 and α_2, the degrees of dissociation of the mercury perchlorates, we have assumed that these salts are dissociated to the same extent as barium perchlorate. This is based on a consideration of the conductivity–dilution curves and hydrolysis data for barium, mercurous, and mercuric perchlorates, which have been determined by Ley and Heimbucher (Diss., Würzburg, 1904). A solution used in these cells (with the exception of cell No. 3) may be considered as being made by the admixture in suitable proportions of two separate solutions, one of mercurous and the other of mercuric perchlorate, the concentration of each being equal to the total salt concentration in the cell; such solutions will be "isoionic" with one another, *i.e.*, the extent of dissociation of the original solutions will not be affected on mixing. Hence by taking the degree of dissociation of barium perchlorate for the total salt

concentration, since $\alpha_1 = \alpha_2$, we can determine $0{\cdot}029\log\alpha_1^2/\alpha_2$ for each cell solution.

Moreover, Ley and Heimbucher have shown that mercurous perchlorate is hydrolysed to the extent of 3—4% in these solutions; and we have shown that mercuric perchlorate is hydrolysed to a similar extent (3%) in $0{\cdot}05N$ solution. Hence the correction to be applied is $0{\cdot}029\log(0{\cdot}97\alpha_1)^2/(0{\cdot}97\alpha_2)$ or $0{\cdot}029\log(0{\cdot}97\alpha_1)$. Now in the solutions that we have studied, $\alpha_1 = 0{\cdot}73$, hence the correction is — 0·0044 volt. It will be seen that the effects of hydrolysis of the perchlorates are of a small order and almost negligible.

Results.

Table I summarises the measurements of nine cells. The observed *E.M.F.*, E_c, of the whole cell is given in col. 7. From this value, the normal oxidation potential E_0 (col. 8) is deduced by substituting the logarithmic correction term (col. 6) in equation (2) and adding the potential of the calomel electrode, 0·560 volt.

TABLE I.

$m = [Hg(ClO_4)_2]$, $n = [Hg_2(ClO_4)_2]$.

Cell No.	m.	n.	m/n.	m^2/n.	$0{\cdot}029\log m^2/n$.	E_c.	E_0.
1	0·0493	0·0431	1·144	0·0564	—0·0407	0·5885	1·1892
2	0·0493	0·0431	1·144	0·0564	—0·0407	0·5882	1·1889
3	0·0049	0·00417	1·175	0·00576	—0·0694	0·5569	1·1863
4	0·0236	0·0670	0·352	0·00831	—0·0647	0·5634	1·1890
5	0·0160	0·0770	0·208	0·00333	—0·0763	0·5540	1·1903
6	0·0121	0·0722	0·168	0·00203	—0·0825	0·5489	1·1914
7	0·0199	0·0707	0·282	0·00561	—0·0697	0·5607	1·1904
8	0·0560	0·0539	1·039	0·05818	—0·0404	0·5902	1·1906
9	0·0581	0·0609	0·954	0·05543	—0·0409	0·5907	1·1916

The results may be divided into two series, since the later cells (Nos. 7, 8, and 9) were made up from slightly different solutions, as previously indicated (see " Preparation of Perchlorates ").

Cell No. 3 was a much more dilute solution, having been prepared by ten-fold dilution of Cell No. 1. In this case, hydrolysis of the mercuric perchlorate is considerable (about 15%), and is probably sufficient to account for the low value of E_0.

The mean *E.M.F.* of these cells (with the exception of Cell No. 3) is 1·1902 volt, with an average error of $\pm$ 0·0008 volt.

The Effect of Perchloric Acid on the Potential.—To determine this, four cells were constructed, by mixing 50 c.c. of a solution in which $[Hg(ClO_4)_2] = 0{\cdot}0687N$ and $[Hg_2(ClO_4)_2] = 0{\cdot}0396N$, with the calculated quantity of $2N$-perchloric acid and sufficient water to make the total volume up to 100 c.c. The following potentials were observed :

TABLE II.

Cell No.	10.	11.	12.	13.
$[HClO_4]$	1*N*	0·5*N*	0·1*N*	Nil.
E.M.F. (obs.)	0·5390	0·5443	0·5728	0·5915

The addition of free perchloric acid to the solution decreases the extent of dissociation of both the perchlorates of mercury, the decrease in the case of the mercuric salt being the predominating factor, because the square of this concentration and only the first power of the mercurous salt concentration enters into equation (2). Thus the observed *E.M.F.* is diminished by addition of perchloric acid. Quantitatively the effect may be expressed thus: substituting the values $[Hg^{\cdot\cdot}] = K_1[Hg(ClO_4)_2]/[ClO_4']^2$ and $[Hg_2^{\cdot\cdot}] = K_2[Hg_2(ClO_4)_2]/[ClO_4']^2$ equation (1) becomes

$$E = E_0 + 0{\cdot}029 \log K_1^2[Hg(ClO_4)_2]^2/K_2[Hg_2(ClO_4)_2][ClO'_4]^2.$$

Since $[Hg(ClO_4)_2]$ and $[Hg_2(ClO_4)_2]$ are constant in the four cells of Table II, these quantities, together with K_1, K_2, and E_0, have been incorporated in a fresh symbol E'_0, and, therefore,

$$E = E'_0 - 0{\cdot}058 \log [ClO_4'].$$

Assuming complete dissociation of both the mercury salts and of the perchloric acid, and taking *E.M.F.* (obs.) = 0·5915 (Cell 13) as a starting point for *E.M.F.* (calc.), the following values of the potentials are calculated:

TABLE III.

Cell No.	10.	11.	12.	13.
$[ClO_4']$	1·11	0·61	0·21	0·11
E.M.F. (obs.)	0·5390	0·5443	0·5728	0·5915
E.M.F. (calc.)	0·5333	0·5483	0·5753	(0·5915)

It is evident that the variation of the potential with perchloric acid concentration can be accounted for satisfactorily, and it is therefore probable that complex-ion formation between the free acid and the salts is either absent or negligible.

It was necessary to show that the potentials measured in this investigation were not due to the perchlorate radical. Experiments were therefore carried out with a platinum-foil electrode dipping into solutions of *N*-perchloric acid and 0·1*N*-potassium perchlorate, respectively. The potentials obtained were ill-defined and in no way resembled those registered in the case of the mercury salts.

Comparison with Previous Data on the Normal Oxidation Potential.

The present investigation gives a value of $E_0 = +1{\cdot}190$ volts on the absolute scale, or ${}_0E_h = +0{\cdot}913$ volt on the hydrogen scale.

The value given in Abegg's "Handbuch der Anorganischen Chemie," [1905, II, (2), 561] is ${}_0E_h = 0{\cdot}87$, obtained by calculation from the normal electrode potential $Hg—Hg_2^{\cdot\cdot}$, ${}_0E_h = 0{\cdot}75$ volt, and the equilibrium relations in the system $Hg—Hg_2^{\cdot\cdot}—Hg^{\cdot\cdot}$, in which the ratio $[Hg^{\cdot\cdot}]/[Hg_2^{\cdot\cdot}] = 235$. This value, 0·87 volt, is probably low, since later determinations of the potential $Hg—Hg_2^{\cdot\cdot}$ (${}_0E_h = 0{\cdot}75$) give a somewhat higher figure; thus Lewis and Randall ("Thermodynamics," 1923, 419) give ${}_0E_h = 0{\cdot}7986$, based on Linhart's measurements, and Abegg, Auerbach, and Luther ("Messungen elektromotorischer Kräfte galvanischer Ketten," 1915, 46) give ${}_0E_h = 0{\cdot}80$. The latter authors have given a value of the normal oxidation potential $2Hg^{\cdot\cdot}—Hg_2^{\cdot\cdot}$, ${}_0E_h = 0{\cdot}92$, which is in good agreement with our experimental results.

Conclusions.

Mercurous and mercuric perchlorates have been prepared and found to be suitable for electrochemical measurements, as their solutions are capable of registering steady potentials with platinum electrodes.

The normal oxidation potential of the process $2Hg^{\cdot\cdot}—Hg_2^{\cdot\cdot}$ is + 1·190 volts.

The effect of free perchloric acid on the potential has been investigated.

The authors desire to express their thanks to the Advisory Council of the Department of Scientific and Industrial Research for a grant to one of them (R. R.) which has enabled him to participate in this investigation.

UNIVERSITY OF BIRMINGHAM,
EDGBASTON. [*Received, November 10th*, 1926.]

XLIV.—*The Adsorption of Benzene Vapour on the Plane Surfaces of Glass, Fused Quartz, and Platinum. The Isosteric Heat of Adsorption of Benzene on Platinum.*

By SAM LENHER.

IT has been previously shown that water vapour is strongly adsorbed on various surfaces at pressures above 95% of saturation (McHaffie and Lenher, J., 1925, **127**, 1559; Lenher, J., 1926, 1785).

The method of measuring the adsorption of benzene on the several surfaces is that described in the above two papers. It consists in obtaining measurements of the change of pressure with temperature

of a vapour at constant volume, using the inside surface of the constant-volume vessel as the adsorbing surface. The following modification was, however, made in the apparatus: the bulb containing the benzene was placed outside the thermostat and a mercury-sealed vacuum-tight tap was used to close it from the apparatus instead of a mercury trap as before.

In all experiments, the adsorption vessel was baked out in a high vacuum immediately before each determination. A furnace consisting of a copper tube wound with nichrome wire and asbestos sheeting was slipped over the adsorption chamber and fixed in position so that the entire tube from the top to the tip of the pointer could be uniformly heated. The furnace was slowly brought to the maximum temperature, which was maintained for 2—3 hours while the vessel was constantly evacuated to 1×10^{-6} cm. The experiment was then begun as soon as the tube had cooled to room temperature.

The benzene used was Kahlbaum's "thiophene-frei" brand. After a thorough drying over phosphorus pentoxide, the benzene was tested for thiophen and gave a negative result. The benzene was distilled after being frozen out twice, the fraction passing over from 80·15—80·20° (standard thermometer) being used. Determinations of the vapour pressure of this benzene gave results agreeing well with those of Dejardin (*Ann. Physique*, 1919, **11**, 253). The saturation pressures determined experimentally agreed excellently with values of the pressure calculated from Dejardin's equation for the vapour pressure of benzene at temperature t, $\log p = 0{\cdot}87476 + 0{\cdot}020670(t - 20) - 755 \times 10^{-7}(t - 20)^2 + 16{\cdot}5 \times 10^{-8}(t - 20)^3$.

The mercury-sealed tap between the bulb of benzene and the adsorption apparatus, and the tap between the vacuum pumps and the adsorption apparatus in the thermostat, were lubricated with metaphosphoric acid prepared by the method of Chapman and Gee (J., 1911, **99**, 1726). In the experiments with a silica vessel, the glass–silica ground joint was lubricated with phosphoric acid before sealing with mercury. The glass, quartz, and platinum adsorption tubes were those used in the earlier parts of this research.

The Adsorption of Benzene Vapour on a Glass and on a Fused Quartz Surface.

Before each experiment, the glass tube was baked out at 250° for 3 hours in high vacuum. Every experiment was done in its entirety at least twice, once from the side of increasing temperature and once from the side of decreasing temperature, to test the complete reversibility of the adsorption equilibrium. This applies also to the experiments with silica and platinum.

In calculating the number of molecules adsorbed per sq. cm. of

surface the equation is the same as that used in the calculations on the adsorption of water on glass, $N/\text{cm.}^2 = (p/T - p_1/T_1) \times 2{\cdot}344 \times 10^{18}$. To express the adsorption in terms of the number of molecular layers (θ), the size of the benzene molecule must be known. Various workers (Jeans, "Dynamical Theory of Gases," 1921; Eucken, *Physikal. Z.*, 1913, **14**, 331; Mack, *J. Amer. Chem. Soc.*, 1925, **47**, 2468; Huggins, *ibid.*, 1922, **44**, 1607; 1923, **45**, 264) give values for the molecular diameter, and $5{\cdot}9 \times 10^{-8}$ cm. has been taken as a probable figure for the mean diameter. Using the square of this value as the area occupied by a single benzene molecule on the surface, the equation from which the number of layers of benzene molecules adsorbed has been calculated becomes $\theta = (p/T - p_1/T_1) \times 8{\cdot}158 \times 10^3$. All the calculations are based on the assumption of a solid surface, plane with respect to irregularities or interstices which would introduce capillary effects of the type considered by Patrick.

As before, the decrease of free energy, $-\Delta F$, of the benzene between the liquid state and that in an adsorbed film is calculated from the usual equation, $-\Delta F = RT \log p/p_1$. The results obtained from five experiments measuring the adsorption of benzene on a glass surface are summarised in Table I. The equilibrium pressures are given in mm. of mercury at 0°:

TABLE I.

Benzene–Glass.

No. 1.					No. 1.				
T K.	p.	$N/\text{cm.}^2 \times 10^{-14}$.	θ.	$-\Delta F$.	T K.	p.	$N/\text{cm.}^2 \times 10^{-14}$.	θ.	$-\Delta F$.
293·9°	78·06	70·30	24·4	0·0	294·8°	79·09	7·03	2·4	18·4
294·0	78·30	51·56	17·9	2·0	295·0	79·23			
294·2	78·57	35·16	12·2	5·6	296·0	79·49			
294·4	78·76	23·44	8·1	9·7	298·0	80·16			
294·6	78·96	14·06	4·8	13·8	300·0	80·88			
		No. 3.					No. 6.		
298·2	95·30	56·25	19·6	0·0	301·1	108·70	56·25	19·6	0·0
298·4	95·63	36·16	12·2	4·8	301·2	109·00	35·16	12·2	3·3
298·6	95·83	23·40	8·1	9·0	301·4	109·24	23·44	8·1	7·6
298·8	96·01	16·41	5·7	13·7	301·6	109·44	11·71	4·1	13·4
299·0	96·18				301·8	109·63			
300·0	96·77				302·0	109·75			
302·0	97·50				303·0	110·20			
					305·0	111·05			
		No. 5.					No. 7.		
299·7	102·23	60·94	21·2	0·0	302·7	116·74	56·25	19·6	0·0
299·8	102·47	44·53	15·5	1·8	302·8	116·98	39·84	13·8	3·2
300·0	102·75	28·12	9·8	5·6	303·0	117·37	14·06	4·9	6·4
300·2	103·00	14·07	4·9	9·9	303·2	117·59	4·68	1·6	10·3
300·5	103·21	7·03	2·4	17·1	303·5	117·74			
301·0	103·48				304·0	118·09			
303·0	104·33				306·0	118·99			
304·0	104·81								

The results show that the equilibrium film which will just exert the saturated vapour pressure of benzene remains of practically constant thickness over the temperature range. The first reading in each series gives the data for this equilibrium film at the saturation pressure. The very low values for the decrease in free energy of the benzene on undergoing adsorption show how little affinity there is between benzene vapour and a glass surface. The data show that adsorption of benzene is measurable only over a temperature range of 0·8° from the saturation temperature, and that the equilibrium pressures of the loosely-held benzene films are practically the saturated vapour pressures. For comparison of these data with other adsorption work, one should consider the figures for the number of molecules adsorbed per sq. cm., for the apparently high values of θ are apt to be misleading, the large results being due to the size of the benzene molecule itself and not to a relatively great adsorption.

The quartz vessel was baked out at 500° for 2 hours in a high vacuum before each experiment. The amount of adsorption was found by use of the equations $N/\text{cm.}^2 = (p/T - p_1/T_1) \times 3{\cdot}395 \times 10^{18}$, and $\theta = (p/T - p_1/T_1) \times 1{\cdot}252 \times 10^4$. The data of five experiments measuring the adsorption of benzene vapour on a pure silica surface are given in Table II.

TABLE II.

Benzene–Silica.

No. 1.					No. 3.				
T K.	p.	$N/\text{cm.}^2 \times 10^{-14}$.	θ.	$-\Delta F$.	T K.	p.	$N/\text{cm.}^2 \times 10^{-14}$.	θ.	$-\Delta F$.
292·0°	71·46	93·48	32·5	0·0	295·3°	83·25	68·21	23·8	0·0
292·2	71·73	64·73	22·5	3·6	295·4	83·61	28·76	10·0	2·7
292·5	72·14	25·16	8·7	8·4	295·6	83·80	14·38	5·0	6·4
292·8	72·37	7·19	2·5	14·9	295·8	84·00			
293·0	72·46				296·0	84·04			
294·0	72·75				298·0	84·94			
296·0	73·23								
No. 2.					No. 4.				
294·0	78·67	71·90	25·0	0·0	297·8	93·62	64·73	22·5	0·0
294·2	78·95	43·14	15·0	2·8	298·0	93·98	28·76	10·0	4·2
294·4	79·20	21·57	7·5	6·4	298·5	94·38			
294·6	79·44				299·0	94·55			
294·8	79·51				300·0	94·98			
295·0	79·56				301·0	95·30			
297·0	80·11								
					No. 5.				
					301·6	111·44	61·11	21·2	0·0
					301·7	111·73	32·35	11·2	0·8
					302·0	111·92	21·57	7·5	8·1
					304·0	112·84			
					306·0	113·52			

These experiments show that the amount of adsorption decreases as the pressure and temperature are increased. This means that the temperature coefficient of desorption is greater than the pressure coefficient of adsorption. The magnitude of the adsorption of benzene on quartz is seen to be almost identical with the measured values for the adsorption on glass (Table I). This is to be expected, for the unsaturated surface forces from glass and from pure silica must be essentially the same as regards their strength in attracting and adsorbing such an indifferent vapour as that of benzene.

The test applied previously of allowing the apparatus to stand at constant temperature (such that adsorption is taking place) for 24 hours or longer, to determine if the equilibrium set up was a stable one, was applied repeatedly in the above experiments. In one experiment (Table II, No. 5), the apparatus was allowed to stand at constant temperature for 4 days; the pressure read at the end of this period was within 0·02 mm. of the initial reading. The equilibrium set up is therefore stable, and over a period of many hours there is no tendency for benzene to penetrate into the bulk of the solid.

The Adsorption of Benzene Vapour on Platinum.

The platinum adsorption tube was made by Messrs. Johnson, Matthey and Co. from burnished seamless platinum tubing. The rounded top end of the tube (see McHaffie and Lenher, *loc. cit.*, p. 1561) was closed by hammering the tube while hot. Before the constricted bottom end was added, the inside of the tube was given a high polish with rouge and chamois. When the narrow bottom end was put on, the tube was filled with rosin to protect the polished surface. After the smaller connecting tube had been worked on to the main adsorption vessel and the rosin had been removed, the inside surface was given a light polish and was carefully cleaned chemically before use.

The equations giving the adsorption are $N/\text{cm.}^2 = (p/T - p_1/T_1) \times 3{\cdot}359 \times 10^{18}$ and $\theta = (p/T - p_1/T_1) \times 1{\cdot}169 \times 10^4$. The tube was baked out at 300° for 2 hours in a high vacuum before each experiment. Table III gives a few of the results of 12 experiments measuring the adsorption of benzene vapour on platinum. It is noteworthy that the adsorption is much greater on platinum than on the surface of silica or glass.

It would have been interesting to continue the experiments at temperatures above 32°, but as the apparatus used was limited to measurements of less than 130 mm., determinations of adsorption at higher temperatures and pressures have been postponed. The results in Table III show that from 295°K. to 300°K. the amount of benzene vapour adsorbed on a platinum surface at the saturation

Table III.

Benzene–Platinum.

No. 1.

T K.	p.	N/cm.^{2} $\times 10^{-14}$.	θ.	$-\Delta F$.
295·4°	83·84	346·0	120·5	0·0
295·6	84·50	275·4	95·9	1·5
295·8	84·96	231·7	80·7	3·9
296·0	85·60	164·6	57·3	4·8
296·5	86·28	104·2	36·2	14·0
297·0	86·88	53·74	18·7	23·5
298·0	87·47			
299·0	87·91			
301·0	88·75			

No. 7.

T K.	p.	N/cm.^{2} $\times 10^{-14}$.	θ.	$-\Delta F$.
299·2°	100·02	453·4	157·8	0·0
299·4	100·78	379·6	132·1	1·6
299·6	101·66	285·5	99·4	1·9
299·8	102·42	211·6	73·6	2·0
300·0	102·98	151·1	52·6	4·2
300·5	103·92	60·47	21·0	12·1
301·0	104·35	26·87	9·3	23·3
302·0	104·90			
303·0	105·44			
304·0	105·86			

No. 3.

295·6	84·60	366·0	127·4	0·0
295·8	85·20	305·6	106·4	2·3
296·0	85·96	225·1	78·3	2·4
296·3	86·79	137·7	49·0	4·3
296·5	87·23	97·40	33·9	7·6
297·0	87·90	36·95	12·8	13·2
297·5	88·23	30·23	10·5	28·8
298·0	88·46			
301·0	89·46			
303·0	90·17			

No. 8.

299·9	103·06	456·7	159·0	0·0
300·0	103·46	403·7	143·8	1·5
300·2	104·24	335·9	116·9	2·7
300·5	105·19	241·8	84·1	5·8
301·0	106·52	110·9	38·5	11·0
302·0	107·62	30·23	10·5	31·8
303·0	108·17			
304·0	108·60			
305·0	109·10			

No. 5.

296·4	87·93	382·9	133·3	0·0
296·5	88·19	349·3	121·6	1·1
296·7	88·79	309·0	107·5	2·8
297·0	89·70	201·7	70·1	4·6
297·5	90·55	124·3	43·2	12·8
298·0	91·25	60·47	21·0	21·8
299·0	91·93	20·15	7·0	44·8
300·0	92·35			
301·0	92·69			
303·0	93·45			

No. 9.

301·3	109·95	399·6	139·1	0·0
301·5	110·82	315·7	109·9	0·9
301·8	111·77	221·6	77·1	3·7
302·0	112·37	161·3	56·1	5·8
302·5	113·34	77·25	26·8	13·4
303·0	113·74	50·38	17·5	25·3
304·0	114·42			
305·0	114·96			
306·0	115·46			

No. 12.

304·0	123·85	268·7	93·5	0·0
304·1	124·21	235·1	81·8	1·5
304·3	124·85	171·3	59·6	3·2
304·5	125·22	151·1	52·6	7·6
305·0	126·08	68·73	23·3	12·9

No. 12.

305·5	126·72	20·16	7·0	35·8
306·5	127·30			
308·0	127·99			
310·0	128·92			

pressure increases with increasing temperature and pressure; and that from 300°K. to 305°K., and perhaps above 305°K., the adsorption falls off rapidly with rising temperature and pressure.

The strikingly large adsorption of benzene on platinum is of great interest, for it is from 5 to 7 times greater than that on glass or silica, and it is slightly greater at certain temperatures than the adsorption of water on silica or platinum.

The Isosteric Heat of Adsorption of Benzene Vapour on Platinum.

The isosteric molar latent heats of adsorption may be calculated from the equation $L = RT^2 d \log p_\theta / dT$ from the measurements of

pressure, temperature, and amount adsorbed given in Table III, where L_θ is the isosteric molar latent heat of adsorption at constant pressure, p_θ, and constant amount adsorbed, θ (see Lenher, *loc. cit.*, p. 1790; Coolidge, *J. Amer. Chem. Soc.*, 1926, **48**, 1795). Values of L_θ for several isotherms at different amounts adsorbed are given in Table IV.

TABLE IV.

L_θ (cals. per mol.).

θ.	297° K.	297·5° K.	298·5° K.	299° K.	299·5° K.	300° K.	301° K.	302° K.
20	—	8440	7790	8070	8790	—	—	—
40	8890	9330	—	8050	8040	—	8140	8190
60	9050	—	8430	—	—	8300	—	—
80	8890	—	8280	—	—	8240	—	8200
100	8450	—	8210	—	—	8000	—	8180
120	8640	—	8110	—	—	—	—	—

The latent heat of condensation of benzene at constant pressure from saturated vapour to liquid varies from 8083 cal. per g.-mol. at 296°K. to 7968 cal. per g.-mol. at 304°K. The isosteric heats of adsorption given above are, within the limits of the accuracy of integration, little different from the latent heats of condensation at the same temperatures. This is in agreement with the results of Lamb and Coolidge (*J. Amer. Chem. Soc.*, 1920, **42**, 1146), who measured the "net" heats of adsorption of many organic liquids on charcoal and found that L_θ was of about the same magnitude as the heat of condensation to liquid. Lamb and Coolidge concluded, from considerations of the heats of adsorption, volume relations in the adsorbed films of different substances, and the area of the adsorbing surface, that the vapours were deposited in a liquid film which was usually many molecules thick. The heats of adsorption of benzene given above, together with the measurements of the vapour pressure of benzene approaching the saturation pressure, are strong evidence that the forces or other causes which bring about adsorption act through a thick multimolecular film.

Discussion.

An explanation was previously outlined (Lenher, *loc. cit.*, p. 1788) which accounted for this pre-condensation adsorption at a solid–vapour interface, and traced the probable course of adsorption on a solid surface over a pressure range from high vacuum to saturated vapour pressure. With very low pressures of the vapour over a perfectly clean surface, the first effect will be the building up of a unimolecular layer of the type which Langmuir has studied on metallic and glass surfaces. The range of pressure over which this primary film is built up is probably quite small, as the great attrac-

tive forces acting from a bare surface must rapidly hold vapour molecules within their range. Carver (*J. Amer. Chem. Soc.*, 1923, 45, 63) found that at 0° a pressure of 0·2176 mm. of toluene vapour caused only 12% of a glass surface to be covered with toluene molecules; in this case, the unimolecular film is still being built up at 3% of the saturation pressure. When a certain definite value of the equilibrium pressure of the adsorbing substance is reached the unimolecular layer will be compact and complete. With further increase of amount, adsorbed films of varying thickness are deposited, perhaps at first with little, if any, change of pressure. A somewhat similar phenomenon has been observed in measurements made recently in this laboratory on the adsorption of various alcohols from aqueous solutions of very low concentrations on active charcoal (Garner, Faraday Society Discussion, October 1, 1926; Knight, unpublished research). We know in the present case that the formation of the multimolecular liquid film does not begin until more than 95% of the saturation pressure is reached. Trouton (*Rep. Brit. Assoc.*,1907, 453; 1911, 328) has observed these two types of adsorption and he estimates the transition pressure to be about 50% saturation in the case of water vapour being adsorbed on a glass surface.

It is of interest to compare the actual thicknesses of the adsorbed films at corresponding pressures, (p_θ/p_w) (p_w is the saturated vapour pressure), as suggested by Williams, in order to follow the variations in the effective range of the attractive force from the surface. The corresponding pressure $p_\theta/p_w = 1$, or saturation, gives the most instructive results. The thicknesses of the saturated equilibrium films of water and benzene on the three surfaces at the highest and lowest temperatures of investigation are summarised in Table V.

TABLE V.

Water Vapour.		*Benzene Vapour.*	
On glass at 25°	$5·3 \times 10^{-5}$ cm.	On glass at 25°	$1·1 \times 10^{-6}$ cm.
On platinum at 20·5°	$6·4 \times 10^{-7}$,,	On platinum at 22·4°	$7·0 \times 10^{-6}$,,
On platinum at 29·5°	$1·1 \times 10^{-6}$,,	On platinum at 26·9°	$9·3 \times 10^{-6}$,,
On silica at 17·8° ...	$4·5 \times 10^{-7}$,,	On platinum at 31°	$5·5 \times 10^{-6}$,,
On silica at 28·4° ...	$1·4 \times 10^{-6}$,,	On silica at 19°	$1·9 \times 10^{-6}$,,
		On silica at 28·7° ...	$1·2 \times 10^{-6}$,,

Assuming that all the adsorption measured takes place on a plane surface, we see that at high vapour pressures, in cases where there is no possible chemical attraction of the primary or secondary valence type, films of the order of 50 to 100 molecular layers are deposited. Apparently even when a liquid is present in bulk at a solid–liquid interface the surface forces from the solid exert a force through many layers of the liquid.

The calculation of the amount of benzene adsorbed on a solid surface rests on the assumption that the Boyle–Charles law, $pv = nRT$, applies to benzene vapour close to the saturation point at ordinary temperatures, and it has been suggested that the foregoing conclusions may be vitiated by the slight deviations of this law from absolute accuracy in the particular circumstances. In the present experiments, the temperature range of the measurements may be divided into two parts for consideration: (1) that region in which the pressure of benzene vapour increases linearly with temperature, and in which the validity of the assumption of the Boyle–Charles law can be tested; and (2) the region in which *apparently* the law is not obeyed, and where the observed deviation from the ideal law is attributed to the adsorption or desorption of vapour from the walls of the containing vessel. That the law holds in the region where there is no measurable adsorption of this type (at temperatures more than 1° above the saturation temperature in the case of benzene) is shown by the following consideration: The Boyle–Charles law states that at constant volume and constant amount of vapour p/T should remain constant; this is verified for benzene vapour, because the value of p/T calculated from the experimental data remains constant within $\pm$ 0·0001, the actual values of p/T in different experiments ranging from 0·2600 to 0·4000. A variation of 0·0001 in the value of p/T from that required by the law would make an error of $2{\cdot}34 \times 10^{14}$ in the number of molecules adsorbed per sq. cm. (N/cm.^{2}), and an error of 0·81 in the value of θ, the number of molecular layers adsorbed. As this possible error is of the same order as the accuracy of measurement, the assumption of the ideal-gas law is justified in this calculation.

In the temperature region from saturation to 1° above saturation, the abnormal increase in pressure above that demanded by the ideal-gas law for the increase of pressure with temperature of a vapour at constant volume is attributed directly to the desorption of vapour molecules from the walls of the vessel. There seems to be no other cause to which this unusual pressure increase may be properly ascribed. Benzene vapour is not an associated vapour which would dissociate on heating slightly (in this case, heating 1°) to give the additional number of molecules to exert the measured increase in pressure. A careful consideration of the possible physical causes of this abnormal pressure rise near the saturation temperature indicates that there are no grounds for doubting the application of the Boyle–Charles law to benzene vapour over the region from saturation to the region where it has been shown that this law is obeyed. From the nature of the problem no more direct test of the applicability of the law to this limited region can be